91602
new 82-10

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THE THIRD ISOTOPE SEPARATION WORKSHOP

Research Report No 89-49-K

H.D. Morrison
Physicist
Science Section
Electrical Research Department

ABSTRACT

The Third Isotope Separation Workshop was held October 5 and 6, 1988 at Ontario Hydro's Conference and Development Centre in Orangeville. Forty-five scientists and engineers from several internationally known research organizations, both in and out of Canada, from Ontario universities, from commercial companies, as well as from Atomic Energy of Canada Limited and Ontario Hydro, met to discuss progress in isotope separation and related activities. Ten of the fifteen presentations involved either hydrogen or zirconium.

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EXECUTIVE SUMMARY

THE THIRD ISOTOPE SEPARATION WORKSHOP

H.D. Morrison
Physicist
Science Section
Electrical Research Department

The series of isotope workshops provides opportunities for Ontario Hydro to discuss its present and future needs for isotope separation with leading researchers in Canadian and foreign research laboratories. At this Third Isotope Separation Workshop, 21 scientists and engineers from Ontario Hydro, including ten from Research Division, met with 24 researchers from universities, national laboratories, and commercial companies to discuss progress in isotope separation, from basic research to commercial development. Ontario Hydro Research Division hosted the meeting October 5 and 6, 1988 at the Conference and Development Centre in Orangeville.

Fifteen presentations were given in two sessions. The first session consisted of two review papers from Ontario Hydro to provide background information on the Corporation's interest in isotope separation. One presentation examined the activities of New Business Ventures Division with respect to isotope sales and services, and the other presentation looked at the Tritium Removal Facility at Darlington.

The second session was devoted to technical papers, mainly on topics related to isotope separation of hydrogen and of zirconium. Four of the presentations were by researchers attending by special invitation: two from the USA, one from Israel, and one from Japan. The remaining papers came from Chalk River Nuclear Laboratories and from Ontario Hydro Research Division.

The discussions on zirconium revealed that four methods of producing zirconium-91 depleted zirconium are still candidates for commercial development. At the time of this report, research is active in only two of these methods. More interest will be generated, however, when a few tens of grams of denatured zirconium can be produced by any method for testing by Ontario Hydro.

Distillation, especially at cryogenic temperatures, continues to be an active research field for separation of isotopes of hydrogen, carbon, oxygen, silicon, sulfur, chlorine, and selenium.

The growing participation in this series of Workshops reflects a continuing need for a forum of discussion on isotope separation and related activities. The next meeting should be held in two years.

89-49

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To Dr. D. Mills
Director of Research

THE THIRD ISOTOPE SEPARATION WORKSHOP

1. INTRODUCTION

The informal setting of Ontario Hydro's Conference and Development Centre was the site of lively discussions during the Third Isotope Separation Workshop, October 5-6, 1988, hosted by Ontario Hydro Research Division. The meeting brought together 45 engineers and scientists for a day and a half to discuss techniques and applications of separation for isotopes of commercial interest. As at the previous workshops, the major elements of interest for isotope separation were hydrogen and zirconium.

This year the Workshop was truly international since we had four invited speakers from around the world: Dr. John Haygarth from Teledyne Wah Chang in the USA, Dr. Jay Hirshfield from Isomed in Israel, Dr. Tom Mills from Los Alamos National Laboratory in the USA, and Dr. Kazuo Takeuchi from the Institute of Physical and Chemical Research in Japan. The other speakers and participants came from Atomic Energy of Canada Limited, Isotec, Lawrence Livermore National Laboratories, MSD Isotopes, National Research Council of Canada, University of Montreal, University of Toronto, University of Waterloo, and Ontario Hydro. All together 15 presentations were given in two sessions. The first session, held in the evening of the first day, consisted of presentations by Ontario Hydro describing some of the applications of isotope separation within the Corporation. The sessions on the second day reviewed progress in techniques for separating isotopes and included a panel discussion on the future of zirconium-91 depleted zirconium, also known as denatured zirconium. The day after the Workshop several attendees took the opportunity to visit the labs at Ontario Hydro Research Division.

The rest of this report provides an overview of the Workshop proceedings for the benefit of those who did not attend. The program of the meeting, listing the contributors and the titles of their presentations, appears in Appendix A. The visual material used in the presentations appears in Appendix B, together with text where provided.

2. SESSION I: ONTARIO HYDRO IN ISOTOPE SEPARATION

The first session began with an introduction and welcome by Dr. Mikk Anyas-Weiss, Manager, Divisional Projects Department in Ontario Hydro Research Division. He outlined why isotope separation is of interest within Ontario Hydro and which Divisions are involved.

The session continued with Mr. Mike Arnold presenting a review of the activities of The Isotope Group, New Business Ventures Division. They are charged with the responsibility of selling isotopes and isotope-related services produced by Ontario Hydro. This includes sales of heavy water, deuterium gas, cobalt-60, and services for upgrading heavy water.

In the final presentation of the session Mr. Bruce Davidson took us on a visual tour of the Tritium Removal Facility at Darlington Nuclear Generating Station, the largest plant for tritium separation in the world. He elaborated on the safety features of the site, then gave us a close-up view of the inner workings of the facility.

3. SESSION II: ISOTOPE SEPARATION TECHNIQUES

The morning half of the second session was devoted almost exclusively to presentations on zirconium. The session began with an invited talk by Dr. Jay Hirshfield from Isomed on their progress in developing a plasma centrifuge for separating zirconium. After a review of the principles of the plasma centrifuge, he discussed the use of a dc vacuum arc for generating the plasma. In tests with chromium, the dc vacuum arc has proved to be well suited to the requirements for economic operation of a plasma centrifuge.

In the second talk, Dr. Hugh Morrison of Ontario Hydro Research Division presented the case for developing atomic vapour laser isotope separation (AVLIS) of zirconium. Recent measurements of the spectroscopy of zirconium performed at the National Research Council have defined feasible pathways for isotope separation. Analysis of a simple process model reveals that AVLIS may well be economic for production of zirconium-91 depleted zirconium.

The third presentation was a departure from isotope separation. Dr. John Haygarth of Teledyne Wah Chang described the production of zirconium from the ore and then addressed the problem of impurities in the metal. Some impurities have beneficial effects on the mechanical and corrosion properties of zirconium. Some other impurities are deleterious and must be reduced as much as possible, or have their effects masked by adding other impurities.

After a short interval of informal discussion, the meeting continued with a panel discussion on the issue of denatured zirconium - where to use it and how much material is needed for the various stages of testing. The leader of the panel was Dr. Ken Woodall of Ontario Hydro Research Division. He was joined by Dr. Craig Simpson of Ontario Hydro Research Division, Dr George Field of Ontario Hydro, Fuel Channel Program Manager for the CANDU Owners Group, Dr. Ed Price of Atomic Energy of Canada Limited, CANDU Operations, and Dr. John Haygarth. Dr. Woodall initiated the discussion which led into candid presentations of the widely varying views held by the panel about the need and applications for denatured zirconium. The presentations prompted several lively interactions with the audience.

The final presentation of the morning session was delivered by Dr. Alistair Miller of Atomic Energy of Canada Limited on a proposed new method for producing heavy water. The method, known as CIRCE, would work in conjunction with a plant for extracting oil from tar sands. The process relies on catalytic exchange between streams of hydrogen gas and water in contact with a wetproof catalyst developed by AECL.

The first talk of the afternoon session was an invited paper by Dr. Kazuo Takeuchi of the Institute of Physical and Chemical Research (RIKEN) in Japan. He reviewed the history of molecular laser isotope separation at RIKEN with respect to separating uranium. Development of a high power Raman laser has proceeded in step with studies of the photochemistry of uranium hexafluoride. They have achieved a separation factor sufficiently high for one-stage enrichment to be practical.

The next three presentations were linked by the theme of laser isotope separation of hydrogen isotopes. Dr. Bob McAlpine of Atomic Energy of Canada Limited reviewed laser isotope separation at Chalk River Nuclear Laboratories with respect to heavy water production and uranium enrichment. Their economic analysis of heavy water production has resulted in a stringent set of criteria for choosing the working molecule to be used in infrared multiphoton dissociation. The search for one or more molecules that meet all the criteria is ongoing. The uranium research is investigating pathways to photoionization for an AVLIS process.

Then, Dr. Glen McRae of Atomic Energy of Canada Limited reported research on a two-colour process for improving the performance of infrared multiphoton dissociation. He has modified a conventional CO_2 laser to operate on $^{13}CO_2$ with two optical resonators. The laser emission of two simultaneous pulses at different wavelengths enhances the multiphoton absorption in deuterated chloroform.

A review of laser-based tritium separation at Ontario Hydro Research Division was presented by Dr. Frank Bartoszek. He described an engineering process diagram of a large-scale system for tritium separation from light water. Cost estimates of this process, which relies on infrared multiphoton dissociation of tritiated trifluoromethane, compare favourably with several more conventional separation technologies.

The next three talks all discussed distillation as a method for isotope separation. An invited talk by Dr. Tom Mills of Los Alamos National Laboratory examined cryogenic distillation as a potentially inexpensive, large-scale method for separation of stable isotopes of silicon, sulfur, chlorine, and selenium. Applications for some of the isotopes are already known, but more applications may develop if they are available at low cost. After illustrating the results obtained on 1-2 m long research stills, he presented colour slides showing the removal of a 200-m long column from its hole in the ground to repair a leak at the bottom.

Then Dr. Ken Woodall of Ontario Hydro Research Division reported on a 1-m long cryogenic still designed for hydrogen isotope separation by distillation of hydrogen. A compact, closed cycle, helium refrigerator provides all the cooling power for the still. The refrigerator eliminates the need for cryogenic fluids, resulting in a tremendous saving in capital and operating costs.

Dr. Jeff Robins of Ontario Hydro Research Division reported on a trial run of separating oxygen isotopes by water distillation. The tests were conducted on one of the finishing units at the Bruce Heavy Water Plant during the summer and fall of 1988. At the time of the Workshop the tests were still ongoing. Starting with reactor grade heavy water at an oxygen-18 concentration of 0.344 atom%, the greatest concentration obtained was 1.26 atom% after 60 days operation under total reflux conditions.

The final presentation of the afternoon session was by Dr. Jim O'Neill of Ontario Hydro Research Division on the application of tunable diode lasers to the problem of detecting isotopes. Lead salt diode lasers, operating at cryogenic temperatures, have long been the only devices capable of sensitive, high-resolution detection of molecules. Recently, communications diode lasers operating near room temperature have been exploited for this task. They are less bulky to use and are built to last 20 years, much longer than lead salt lasers.

4. CONCLUSIONS

The Third Isotope Separation Workshop brought together an international group of scientists and engineers to discuss a wide variety of topics related to isotope separation. The attendance was greater than at either of the two previous Workshops, while the number of presentations remained about the same as the last time. The increased participation in this Workshop reflects a continuing need for a forum of discussion on isotope separation and related activities. To fulfil this need, either the Workshop series should continue or a similar meeting should be held in conjunction with a larger conference. At the current pace of research and development in this field, a meeting every two years would be sufficient.

5. ACKNOWLEDGEMENTS

It is a pleasure to thank all those who attended the Third Isotope Separation Workshop, especially to those who made presentations of their work and provided the material for Appendix B.

Approved:

A.F. Baljet
Manager
Electrical Research Department

Submitted:

H.D. Morrison
Physicist
Science Section

APPENDIX A

THIRD ISOTOPE SEPARATION WORKSHOP

October 5-6, 1988

Ontario Hydro Conference and Development Centre
Orangeville, Ontario

Wednesday, October 5

Workshop I: Background

Chairman: Hugh Morrison, Ontario Hydro Research Division

1. Introduction and Welcome

   Mikk Anyas-Weiss - Ontario Hydro Research Division

2. Ontario Hydro's Isotope Marketing Program
   Mike Arnold - The Isotope Group
   New Business Ventures
   Ontario Hydro

3. The Tritium Removal Facility at Darlington
   Bruce Davidson - Operations - Darlington NGS
   Ontario Hydro

4. International Isotope Society: A Canadian Chapter?

   Open Discussion led by Mike Arnold, Ontario Hydro

Thursday, October 6

Workshop II: Separation Techniques

PART A

Chairman: Craig Simpson Ontario Hydro Research Division

1. Plasma Centrifuge for Zirconium Separation
   Jay Hirshfield - ISOMED, Israel

2. Separation of Zirconium Isotopes
   Hugh Morrison - Ontario Hydro Research Division

THIRD ISOTOPE SEPARATION WORKSHOP

3. Zirconium: Separation, Influence of Impurities on Properties, Impurity Removal and Analysis
   John Haygarth - Teledyne Wah Chang, Oregon

4. Denatured Zirconium: Where do we go from here?
   Panel Discussion led by Ken Woodall, Ontario Hydro Research Division

5. Heavy Water Production by the CIRCE Process
   Alistair Miller - AECL, Chalk River

PART B

Chairman: Sav Sood - Design & Development - Gen Ontario Hydro

6. Molecular Laser Isotope Separation at RIKEN
   Kazuo Takeuchi - Institute of Physical & Chemical Research, Japan

7. LIS Studies at Chalk River Nuclear Laboratories
   Bob McAlpine - AECL, Chalk River

8. Two-Colour $^{13}CO_2$ Multiphoton Absorption of $CDCl_3$
   Glen McRae - AECL, Chalk River

9. Tritium Separation by Laser
   Frank Bartoszek - Ontario Hydro Research Division

10. Separation of Silicon, Sulfur, Chlorine and Selenium Isotopes by Distillation
    Tom Mills - Los Alamos National Laboratory New Mexico

11. Low Cost Hydrogen Isotope Separation
    Ken Woodall - Ontario Hydro Research Division

12. Oxygen Isotope Separation
    Jeff Robins - Ontario Hydro Research Division

13. Use of Tunable Diode Lasers as Sensitive Detectors of Isotope Ratios
    Jim O'Neill - Ontario Hydro Research Division

14. Summary and Discussion
    Hugh Morrison - Ontario Hydro Research Division

APPENDIX B

THIRD ISOTOPE SEPARATION WORKSHOP

SUMMARY OF PRESENTATIONS

OPENING REMARKS FOR THIRD ISOTOPE SEPARATION WORKSHOP

N. Anyas-Weiss
Ontario Hydro Research Division

It gives me great pleasure to welcome you to the Third Isotope Separation Workshop. I want to extend a particularly warm welcome to those of you, and I can recognize several familiar faces, who have participated in the previous workshops. Those of you who are here for the first time, I hope to see at future workshops of this kind. Given the number of you here tonight, the First Workshop held in 1984, was quite a modest affair. Also, given that we have contributions from Israel and Japan, I would feel justified in putting the modifier INTERNATIONAL into the title.

For Ontario Hydro much has changed in the four years since the first workshop. For example, the tritium recovery facility being started then at Darlington has been completed and we have been given permission to transport tritiated water from our Pickering Plant to Darlington. The Corporation has taken a much keener interest in the production and sale of a variety of isotopes, notably deuterium, tritium, carbon-14, oxygen-18, and cobalt-60. You will hear more about both of these topics in this evenings session.

At AECL a new program in Laser Isotope Separation of deuterium has been started and in both organizations thee is an increasing interest in the use of ^{91}Zr depleted zirconium for new reactor designs.

I want to deal in a little more detail with Ontario Hydro's interests in isotopes and isotope separation. This workshop, as the previous ones, is organized by the Research Division, which has been involved in isotope separation for the past 15 years. Our concern has been to look at alternate and more economic ways to separate deuterium, tritium and carbon-14.

Our New Business Venture Division has the task of selling the isotopes produced by Hydro and to developing new markets for our isotopes and isotope related products.

Hydro's Design & Development Division has an interest in isotopes because they are involved in the design of heavy water and tritium recovery plants, as well as our reactors and sub-systems.

Hydro's Operations is vitally interested, because they run the plants and deal with all of the processes which generate the various isotopes. They are interested in producing in an efficient way an acceptable product.

The international interest in isotope separation is borne out by your attendance here at this unique workshop, one totally dedicated to isotope separation methods. In the future I see an even greater emphasis on isotope separation, as we find that the availability of ultra-pure elements and isotopes underlies the advance of such technologies as supercomputers and superconductivity

and medical diagnosis. Although we have come a long way in the isotope separation business, I think that we have just started to tap a few of the opportunities.

Therefore, I look forward, during this workshop, to a stimulating exchange of ideas and the emergence of ideas and directions. This workshop is also an opportunity to make new contacts and renew old ones, both of which will sustain us through the periods of challenging research ahead. So I invite you to participate, challenge, contribute, but most of all, to enjoy the opportunities of a shared interest.

ONTARIO HYDRO'S ISOTOPE MARKETING PROGRAM

M. A. Arnold
The Isotopes Group
New Business Ventures Division
Ontario Hydro

Ontario Hydro is a Corporation created by a special statute of the Province of Ontario in 1906. It operates under the Power Corporation Act with broad powers to generate, supply and deliver electric power throughout the province. Ontario Hydro is one of the largest and most technically advanced public utilities in North America. In 1987 over 3 million customers were served by Ontario Hydro. Their electric power needs were met by a generation mix of nuclear (50%), fossil (25%) and hydraulic (25%) generating plants totalling 30, 000 MWe of installed capacity.

Ontario Hydro is an internationnal leader in the production of isotopes from nuclear facilities. Marketing these isotope by-products is the main function of The Isotopes Group.

Cobalt-60 is one of today's most useful radioactive isotopes employed throughout the world in cancer therapy, medical product sterilization and in such emerging technologies as the treatment of food to reduce spoilage, and the sterilization of toxic waste sewage, and bacterial or viral waste. In 1987, Ontario Hydro sold almost 90% of the world supply, making it the world's leading supplier.

Now in its third year of commercial production, deuterium gas is one of Hydro's newest products. The principal applications of deuterium gas lies in fusion technology, chemical processes and medical research. Deuterium sales were very robust in 1987, continuing to increase market share as in previous years.

The department also enjoyed considerable success in the heavy water market with shipments of 12 tonnes to 18 clients in six different countries. The dominant reason behind Hydro's competitive success in the heavy water market resides in its commitment to service and the purity of the product it delivers. Hydro is the only bulk producer able to meet a 99.99% isotopic purity level with virtually zero tritium contamination.

The Isotope Group is currently exploring new deuterium applications. One promising area involves using heavy water for replacing hydrogen with deuterium in chemical compounds to make them more stable by increasing their resistance to oxidation. The functional capability of lubricants for instance, can be increased by deuteration.

Other research initiatives are also underway in such areas as Helium-3 and Oxygen-18. All these efforts will ultimately make Ontario Hydro not merely a bulk supplier of isotopes, but also a market oriented manufacturer commanding a full range of isotopic products and services.

THE TRITIUM REMOVAL FACILITY AT DARLINGTON

B. Davidson
Operations - Darlington NGS
Ontario Hydro

(C)

Oct. 1988 (R-3)

PRESENTATION DARLINGTON NGS

TRITIUM REMOVAL FACILITY

TRF

TRF HAZARDS

1. No fission products in TRF

2. Hydrogen isotopes - H_2

   - D_2

   - T_2 - Beta emitter
     1/2 life 12.5 years

3. HTO, DTO is approximately 20,000 times more hazardous than elemental T_2

R.B. Davidson 88/10/4

R.B. Davidson
Commissioning Superintendent
Darlington NGS-A-TRF

TRF PRESENTATION ON DESIGN/COMMISSIONING AND OPERATION

1. Overview of Design

   Reasons TRF Built

   - Man Rem reduction for Operators, Mechanical Maintenance, Control Technicians.
   - Lower release of T2 to the environment.
   - T2 sales (not approved yet).
   - Scaled up from I.L.L., Grenoble, France (size 3 X, production 25 X)
   - Designed to handle Reactor Grade water (clean up/no fission products).
   - Lower isotopic will reduce production.
   - Moved TRS from Pickering NGS to Darlington NGS TRF, February 1983.
   - In commissioning phase I now.
   - 4 Design/Construction packages
     - Pkg #1 - Sulzer (approximately 18 subsystems)
     - Pkg #2 - Koch (AES, GBCS)
     - Pkg #3 - OHR (TIS) & NMMD (TAP)
     - Pkg #4 - DED (includes HWMB)

2. TRF Operational Safety
3. TRF Design Safety
4. TRF Safety Analysis
5. SLIDES of the TRF systems.

(2)

ISE FEATURES

- UNIQUE TO ONTARIO HYDRO/CANADA
- WIDE VARIETY OF PROCESSES
- STATE OF THE ART CONTROL SYSTEM
- UNIQUE SIGNIFICANT SAFETY IMPLICATIONS
- DESIGNED TO IMMOBILIZE T_2 ON TITANIUM SPONGE (IMMOBILIZATION TRITIUM CONTAINERS - ITC)
- PRIMARY FUNCTION TO REDUCE MREM UPTAKE BY OPERATING PERSONNEL

PR14

Figure 6 Moderator System

Tritium Activity

1986-1990

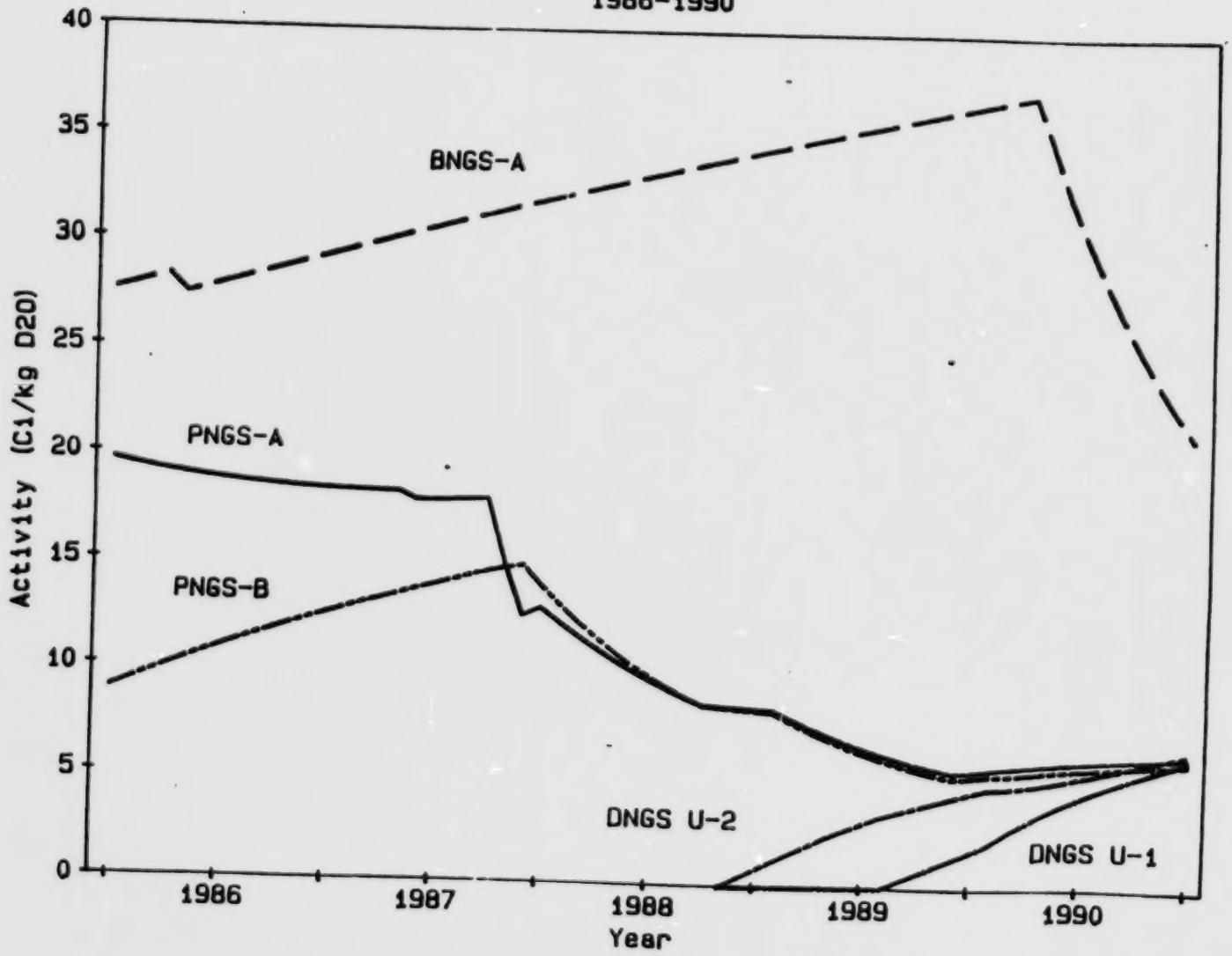


Figure 9a

PNGS-B PREDICTED TRITIUM INTERNAL DOSE

1986-1991

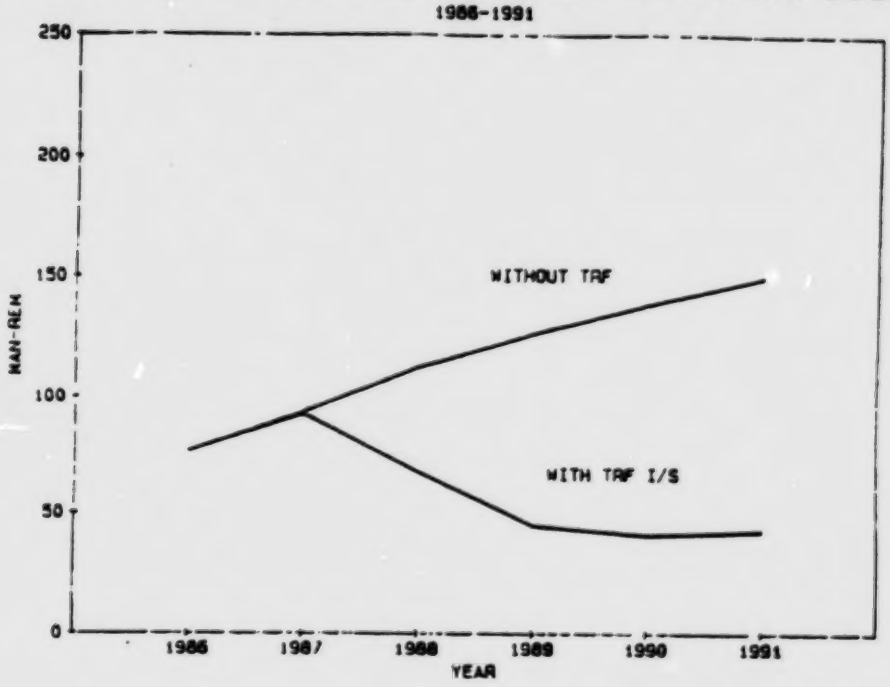
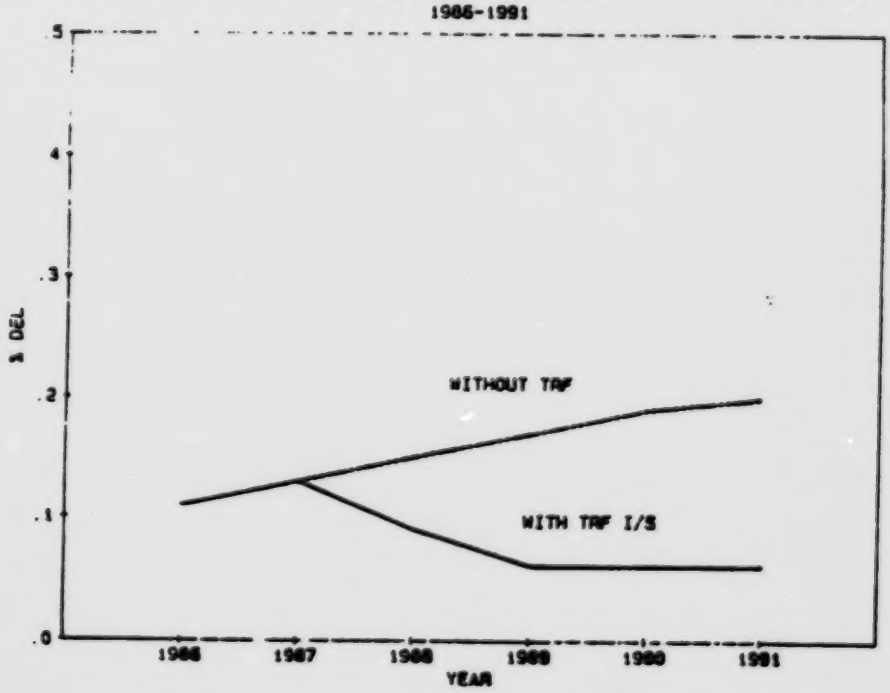
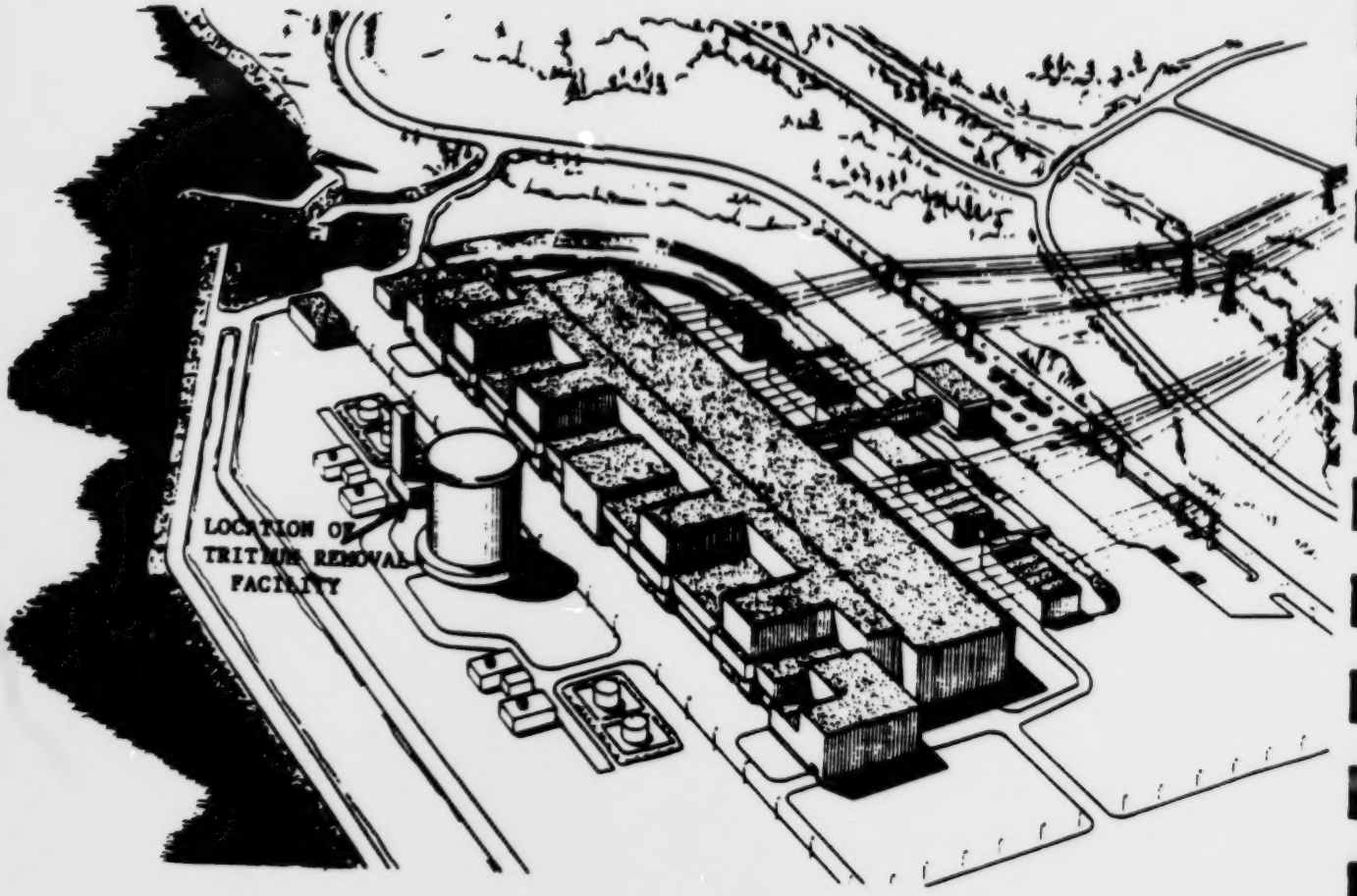


Figure 9b

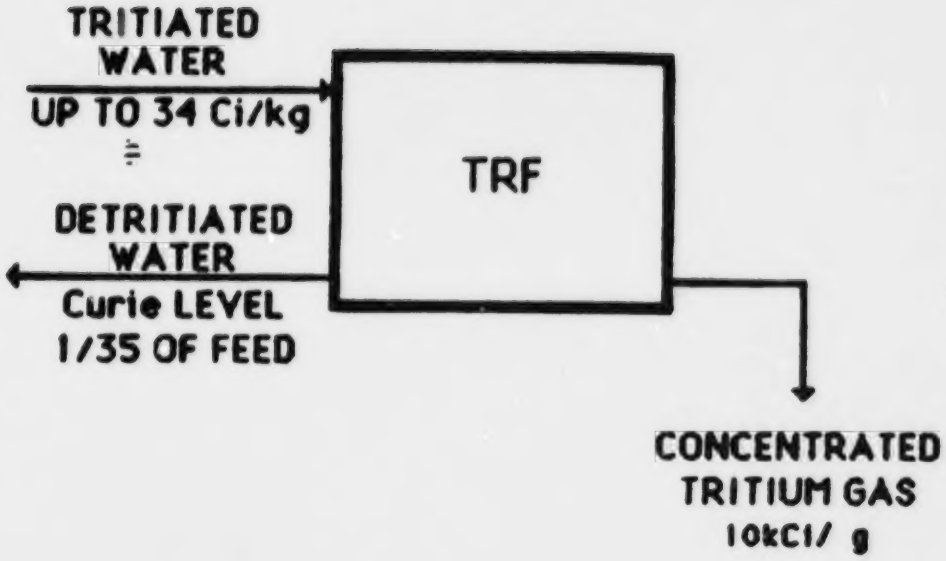
PNGS-B PREDICTED AIRBRONE H3 EMISSIONS

1986-1991



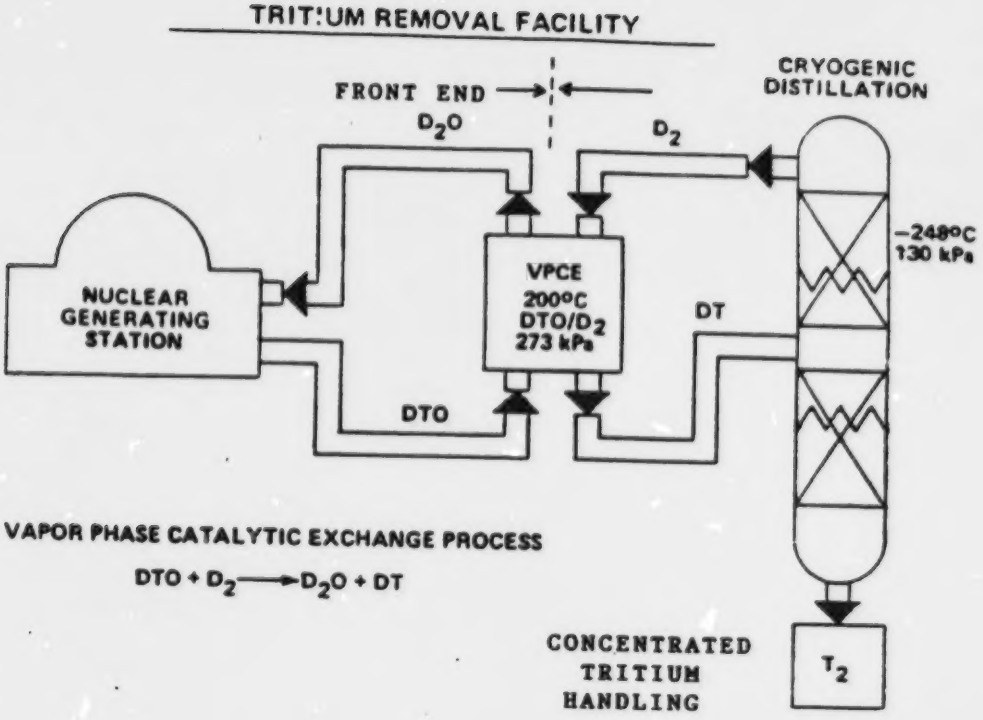

LOCATION OF
TRITIUM REMOVAL
FACILITY

MAIN INPUTS & OUTPUTS

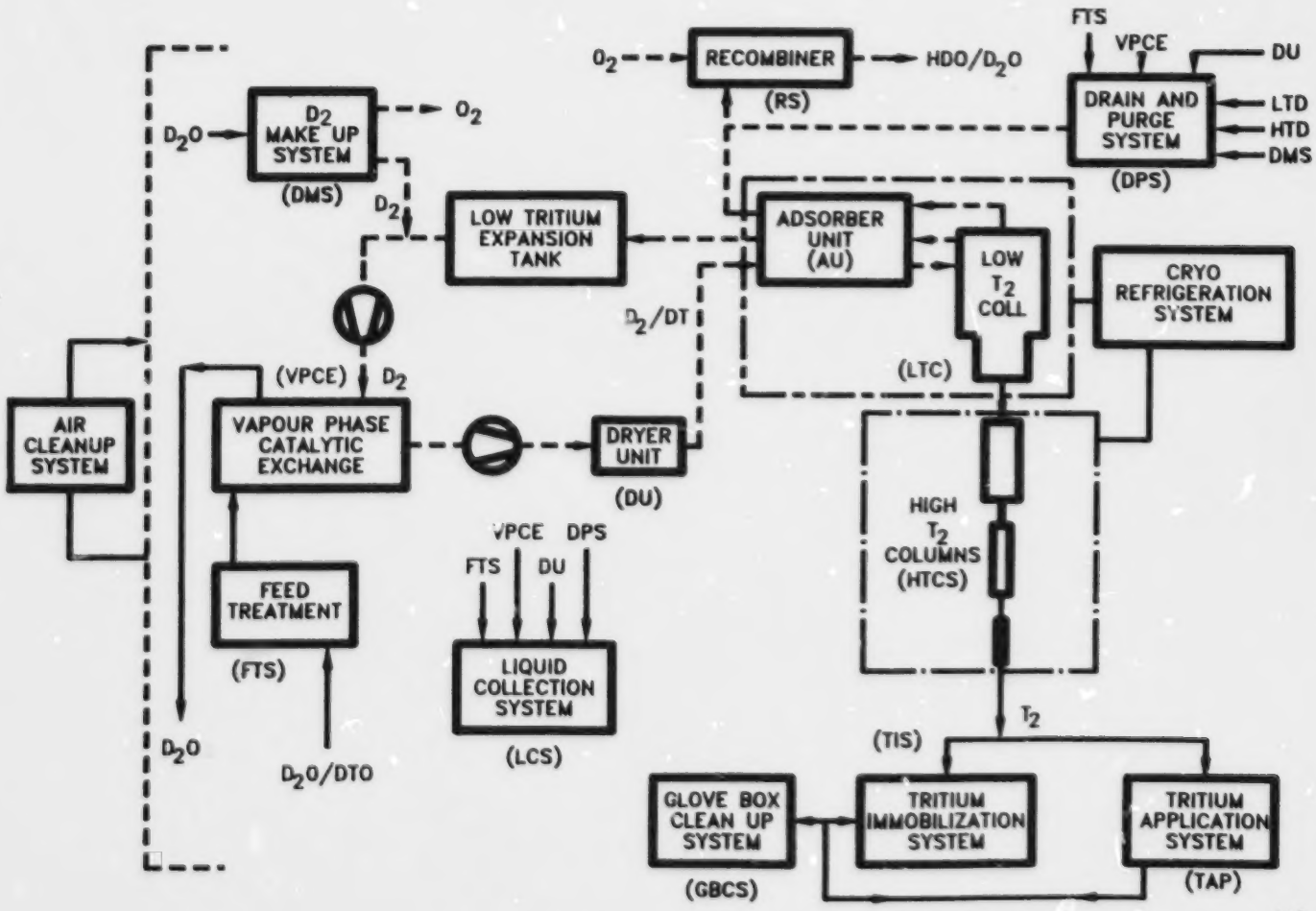


(1)With initial feed 34 Ci/Kg - 80 MCi per year

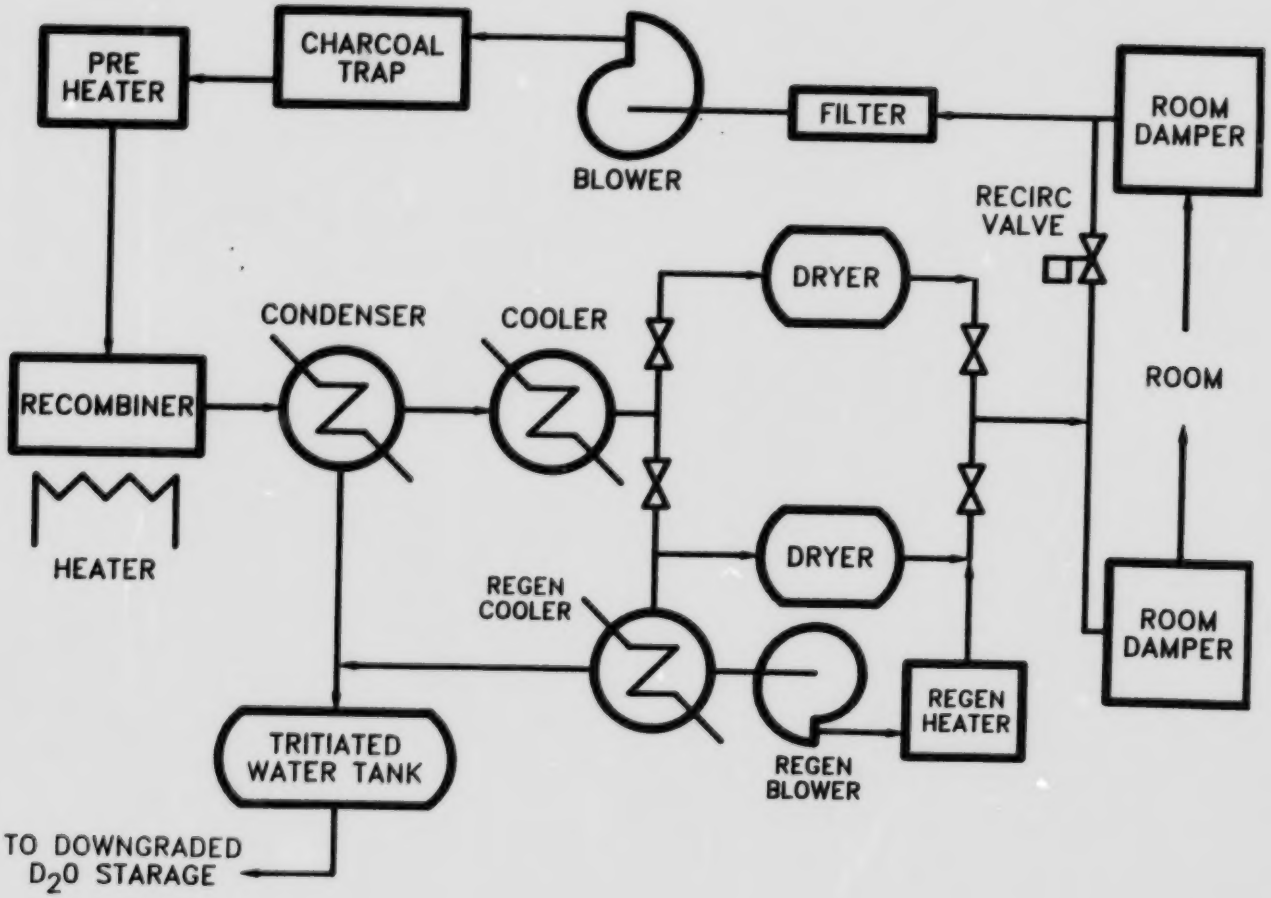
(2)With equilibrium feed 10 Ci/Kg - 10 MCi per yea


TRITIUM REMOVAL FACILITY
FRONT END
D_2O
D_2
CRYOGENIC DISTILLATION
NUCLEAR GENERATING STATION
VPCE
200°C
DTO/D_2
273 kPa
DT
DTO
-248°C
130 kPa
VAPOR PHASE CATALYTIC EXCHANGE PROCESS
$DTO + D_2 \longrightarrow D_2O + DT$
CONCENTRATED TRITIUM HANDLING
T_2

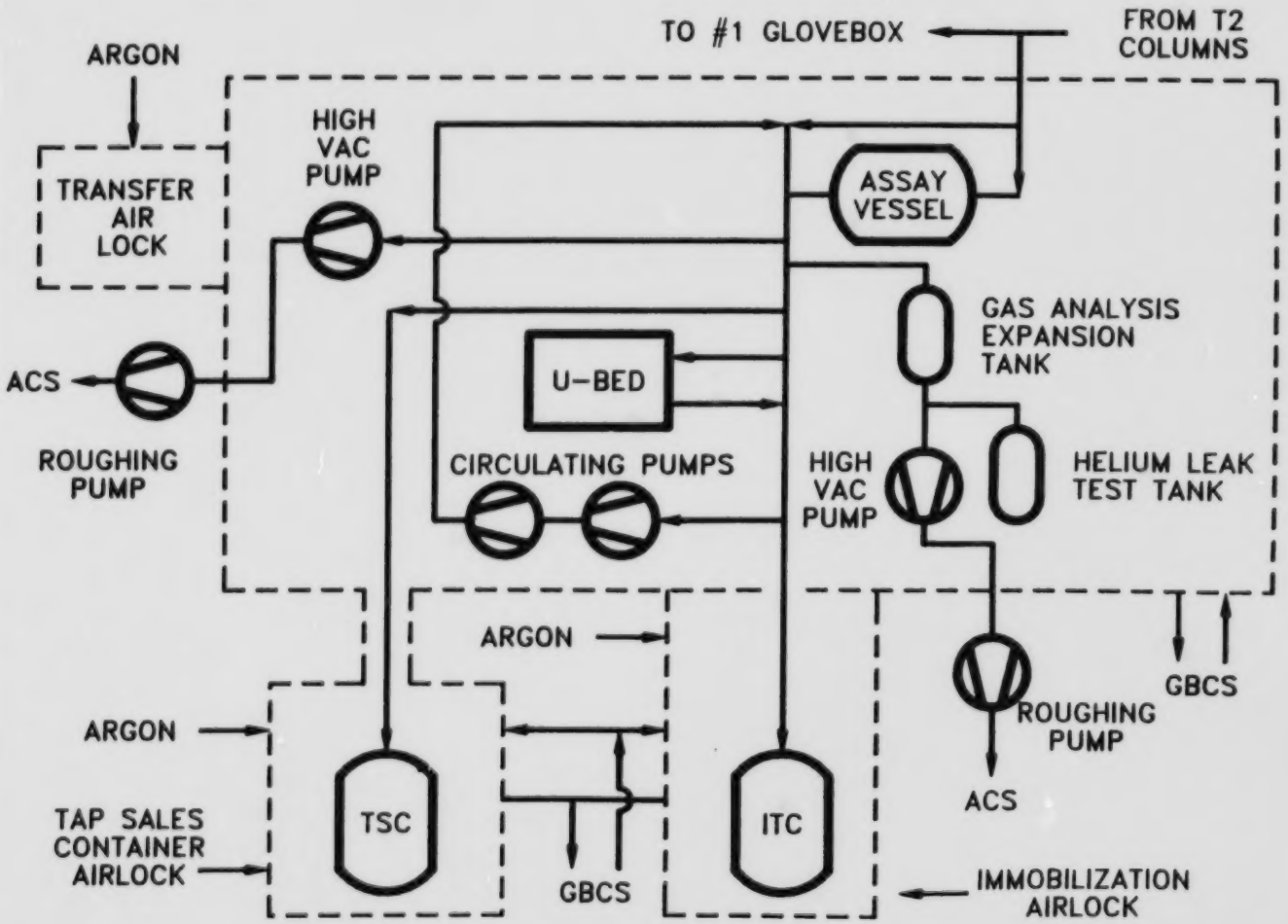
DTRF – SIMPLIFIED FLOW DIAGRAM



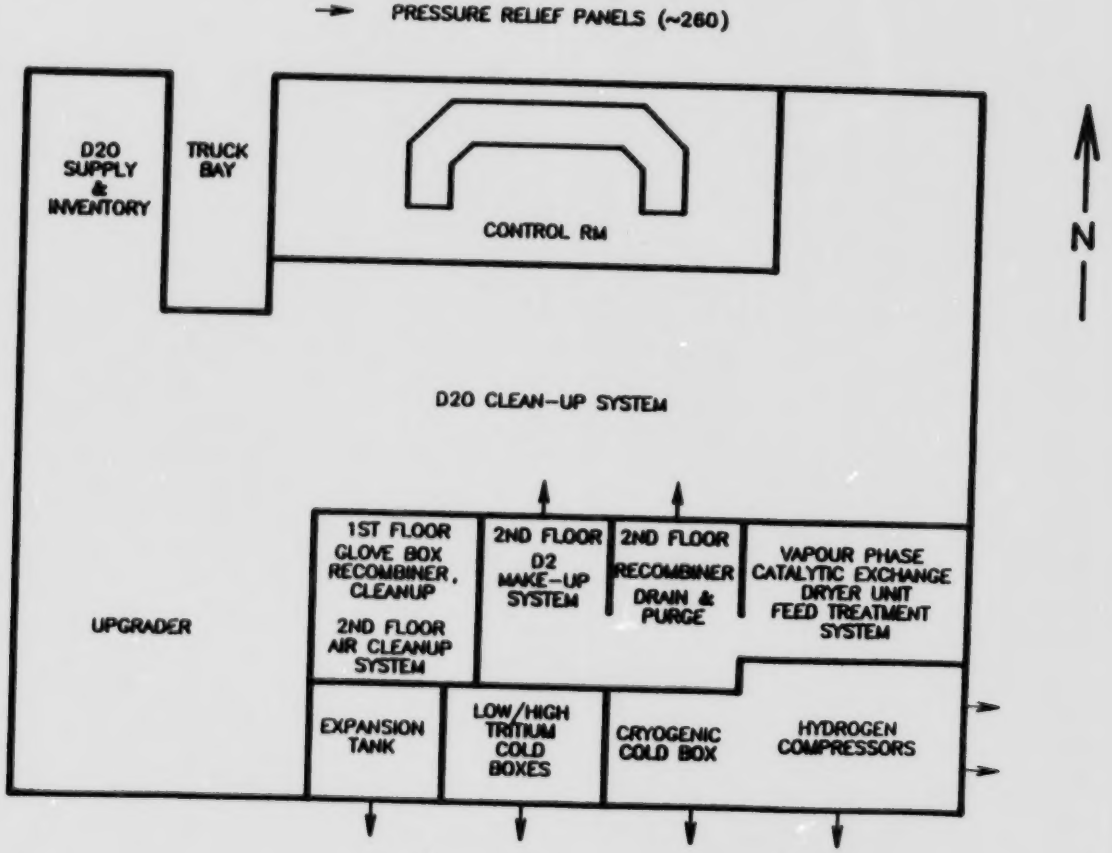
AIR CLEAN UP SYSTEM (ACS)



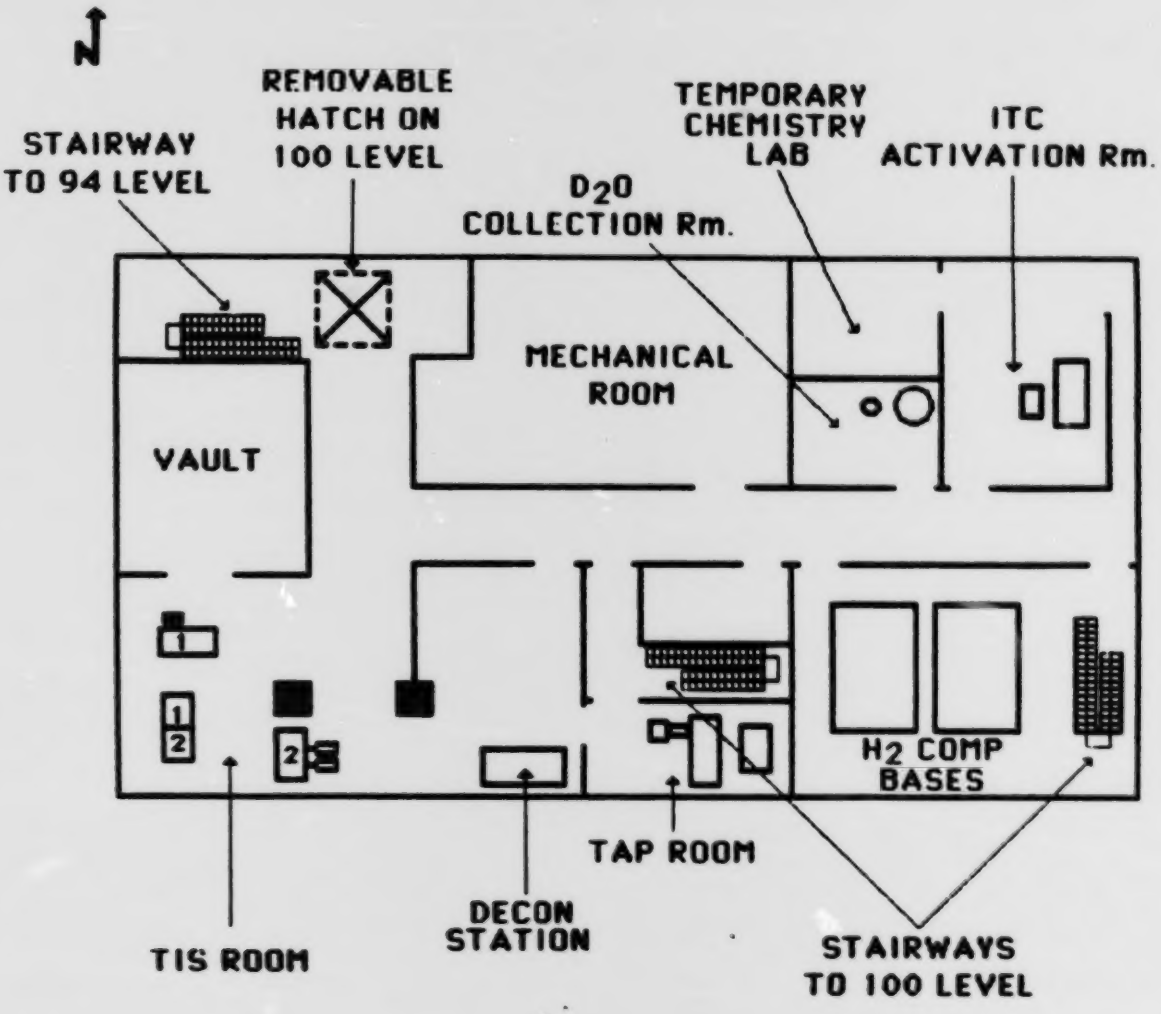
TRITIUM IMMOBILIZATION SYSTEM (TIS)



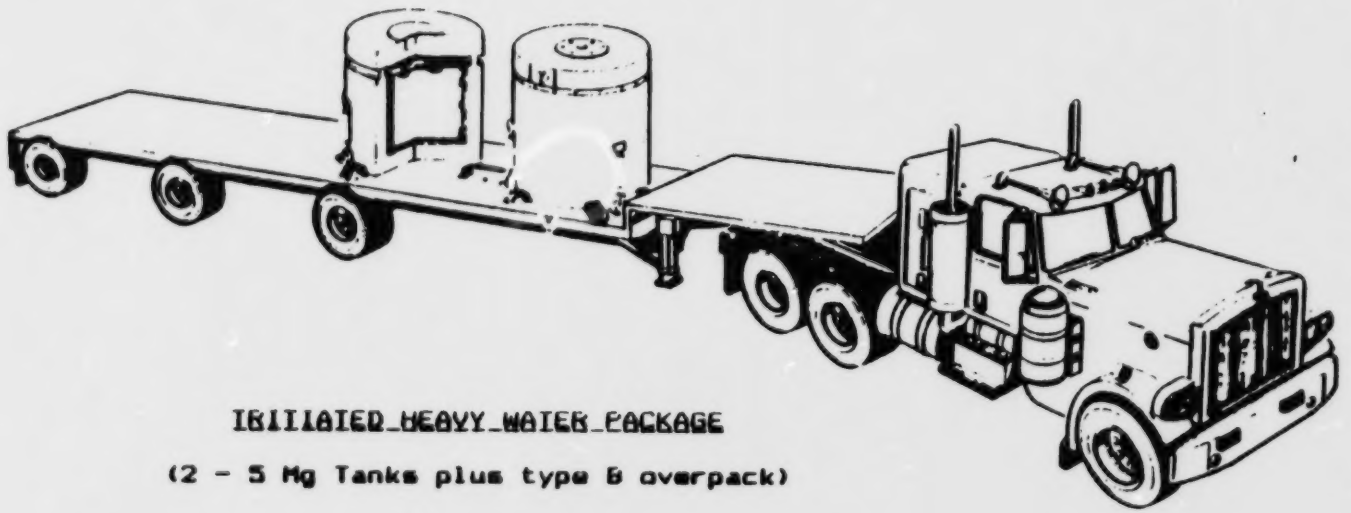
HEAVY WATER MANAGEMENT BUILDING AND TRITIUM REMOVAL FACILITY



hwb.trf



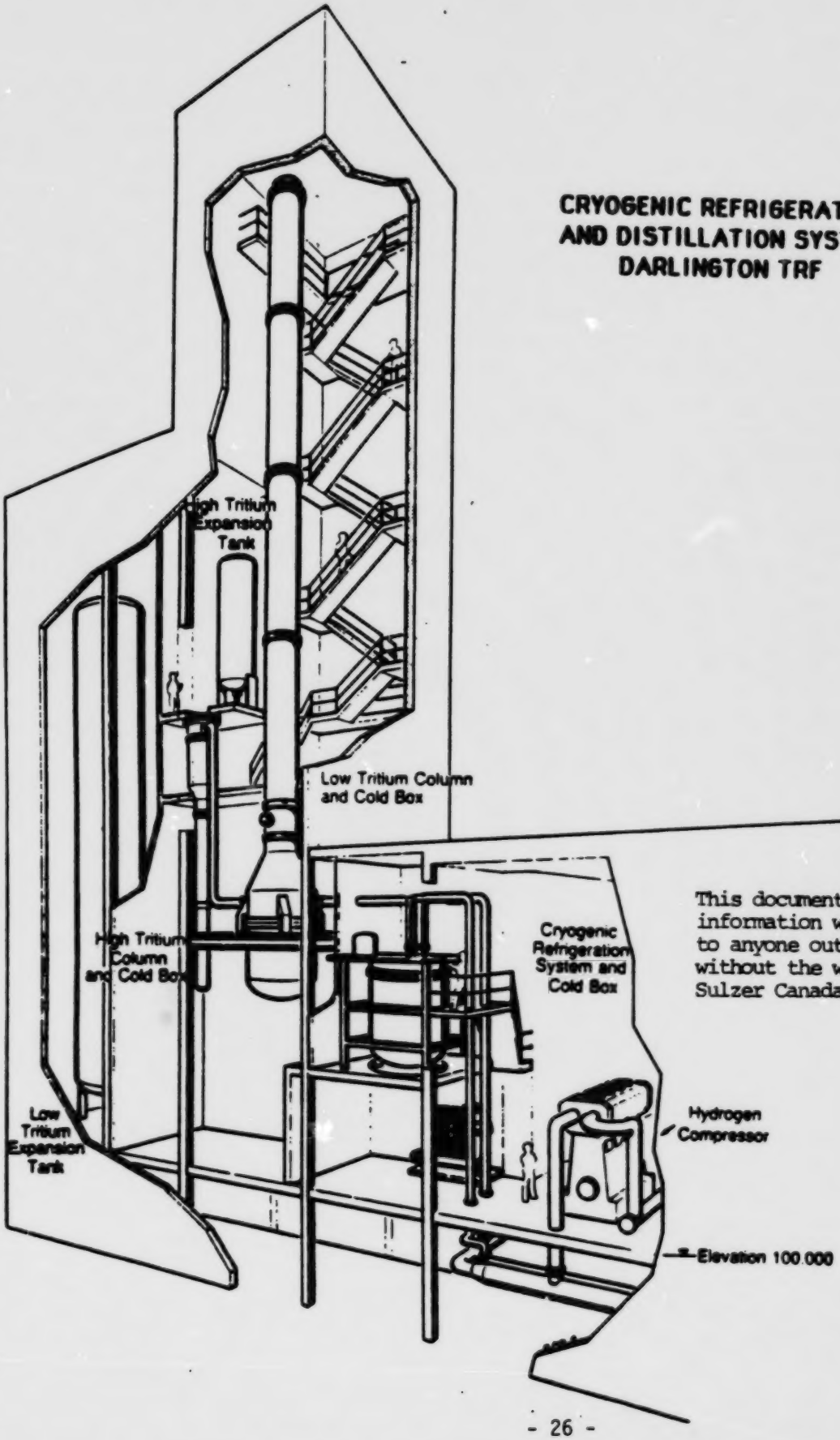
FLOOR PLAN - TRF BASEMENT



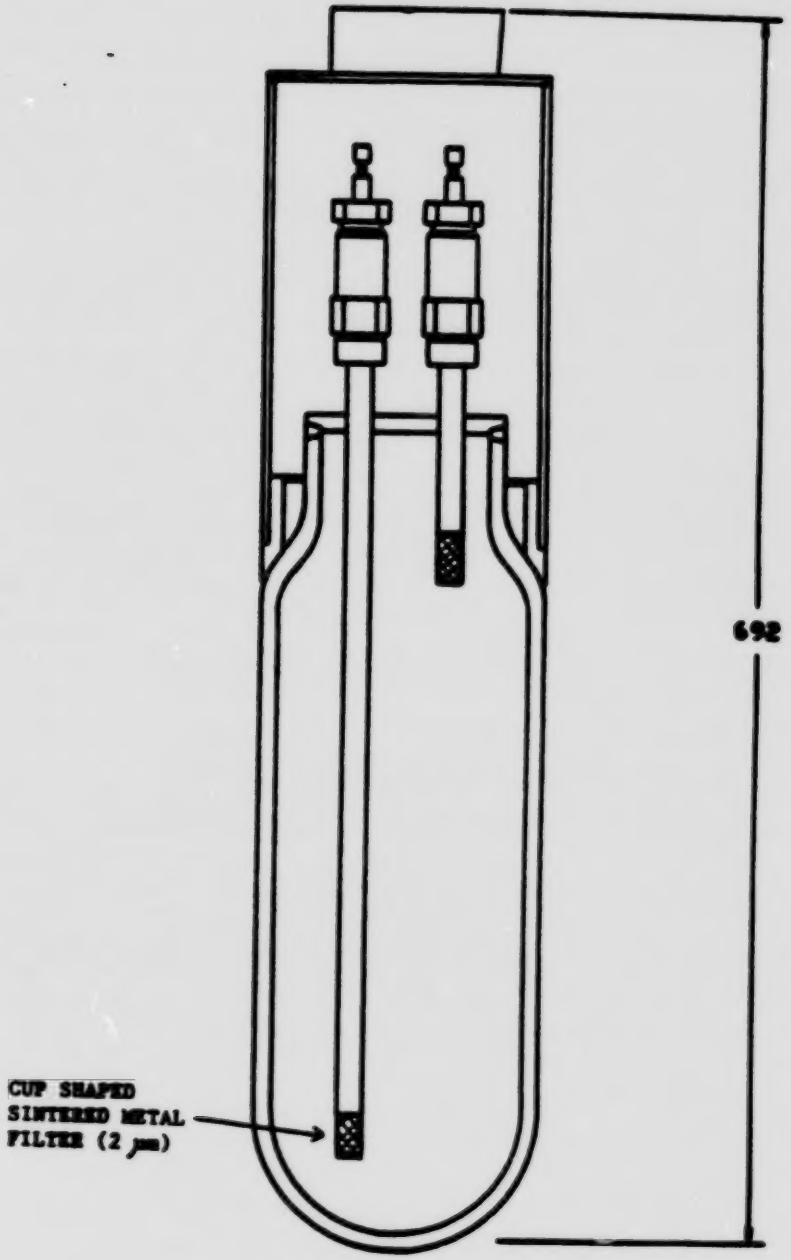
IRRIDIATED HEAVY WATER PACKAGE

(2 - 5 Mg Tanks plus type B overpack)

CRYOGENIC REFRIGERATION AND DISTILLATION SYSTEMS DARLINGTON TRF

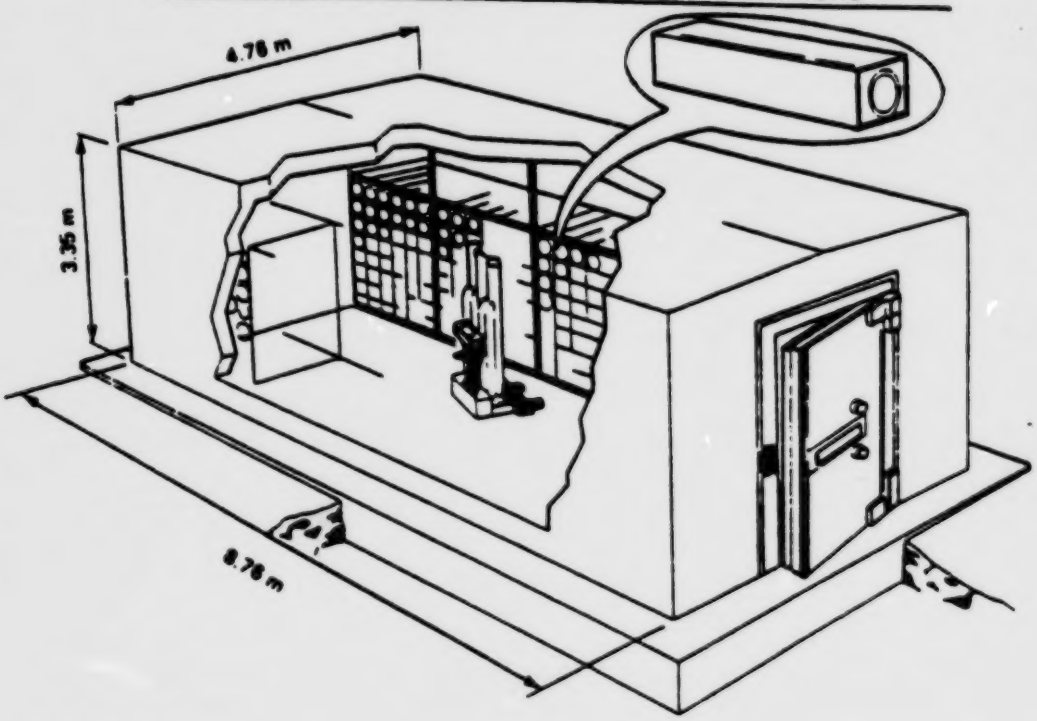

High Tritium Expansion Tank
Low Tritium Column and Cold Box
High Tritium Column and Cold Box
Cryogenic Refrigeration System and Cold Box
Low Tritium Expansion Tank
Hydrogen Compressor
Elevation 100.000

This document contains proprietary information which cannot be released to anyone outside Ontario Hydro without the written agreement of Sulzer Canada Inc.

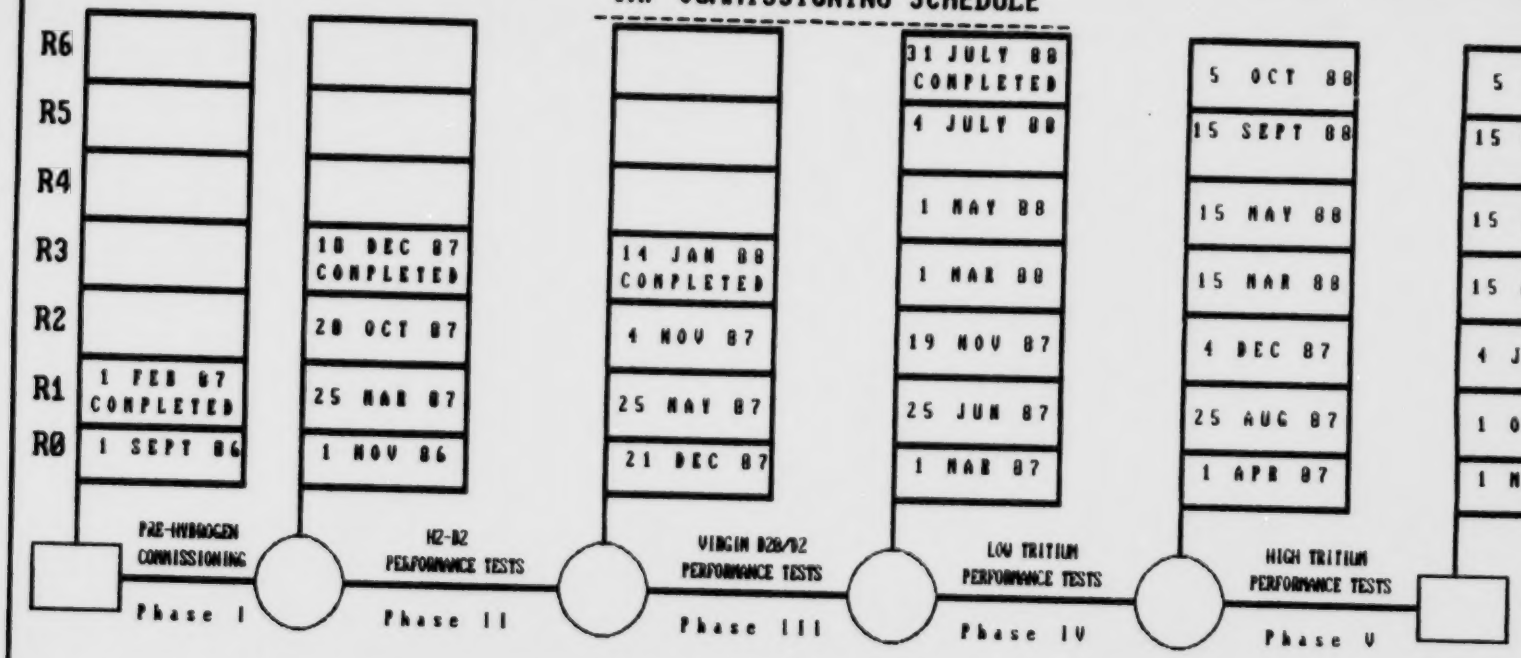


IMMOBILIZED TRITIUM CONTAINER

RACKS FOR STORAGE OF TRITIUM CONTAINERS



TRF COMMISSIONING SCHEDULE



Major Delays:

- **R0 (May 86)** – Original Forcast
- **R1 (Feb 87)** – Construction Late Turnovers
- **R2 (Sept 87)** – LRC Failures / Vibrations
  - Oxygen Removal Problems
- **R3 (Jan 88)** – LRC Vibrations
  - H2 Purifier Modifications
  - LT1604 Replacement
  - TE3111 Repair
  - DMS Reliability
  - DPS & Recombiner Problems
- **R4 (Apr 88)** – TIS Problems
  - TDO Package Re-Licencing
  - TE3111 Replacement
- **R5 (Jun 88)** – Operator Loading D2 into ITCs
  - D2 Conditioning of Pipework
  - Replace UPCE Pipe Saddles
  - Repair CP1201
- **R6 (Sept 88)** – CP1201 spare parts
  CP3401 LPSW trips
  GBCS commissioning

TRF – COMISSIONING MILESTONES

PREPARED BY: K.E. Juggett

VERIFIED BY:

APPROVED BY: R.B. Dunbar 88/9/30

DATE: 88/09/30 REVISION: 6

TRF SAFETY

POTENTIAL HAZARDS

- HYDROGEN ISOTOPE FIRE/EXPLOSION
- TRITIUM OXIDE (TRITIATED D2O)
- ELEMENTAL TRITIUM

IN PERSPECTIVE

TRF HAZARD		COMPARISON
REFRIGERATION SYSTEM	500 m^3 H2	DNGS GENERATOR 130m^3 H2
TRF PROCESS	1500 m^3 D2	
TOTAL	2000 m^3	

- INVENTORY OF TRITIATED D2O
  20 Mg AT UP TO
  34 Ci/Kg

  BRUCE MODERATOR SYSTEMS
  APPROX. 350 Mg AT 26
  Ci/Kg

- POTENTIAL FOR SMALL QUANTITIES OF HIGHLY TRITIATED WATER

- CONCENTRATED TRITIUM GAS
  99.9% PURE, 45KCi BATCHES

  - NO SIMILAR HAZARD IN
  - ONTARIO HDYRO
  - MANY FACILITIES IN US AND EUROPE HANDLE CONCENTRATED TRITIUM
    EUROPE HANDLE
    CONCENTRATED TRITIUM

SAFETY PHILOSOPHY

I. ELIMINATE HAZARDS THROUGH GOOD DESIGN

II. MINIMIZE HAZARDS THROUGH SOUND OPERATING PROGRAMS

III. DEAL WITH IMMEDIATE HAZARDS WHEN THEY ARISE

I. ELIMINATE HAZARDS THROUGH GOOD DESIGN

DESIGN FEATURES THAT WILL CONTRIBUTE

TO THE SAFE OPERATION OF TRF

1. OPERATE SLIGHTLY ABOVE AMBIENT PRESSURE

2. INVENTORIES MINIMIZED

3. CRYOGENIC COLD BOXES DOUBLE CONTAINMENT, MONITORED VACUUM INTER SPACE, AUTOMATIC SHUTDOWN ON DETECTION OF T_2/H_2

4. SUB SYSTEMS ISOLATED

   SUB SYSTEMS GROUPED TO MINIMIZE TRITIUM CONTENT IN A GIVEN ROOM

5. T_2 LOSSES MINIMIZED WITH COLD TRAPS

6. WELDED PIPING
   VESSEL FLANGES ARE SEAL WELDED
   H_2 REFRIGERANT GROOVED O RING DESIGN

7. PROCESS CONTROL HAS 100% BACK UP

8. AREA ALARMING TRITIUM MONITORS STRATEGICALLY LOCATED

9. HIGH CAPACITY VENTILATION

   ACS, GBCS DETRITIATE INDIVIDUAL ROOMS AND GLOVE BOXES RESPECTIVELY

10. ELECTRICAL EQUIPMENT CLASS I DIVISION II GROUP B

11. FIRE FIGHTING EQUIPMENT HOSE CABINETS/PORTABLE EXTINGUISHERS

    I/R THERMAL FLAME DETECTOR

12. LOSS OF CLASS IV POWER, RESULTS IN SAFE SHUTDOWN. PRESSURE INCREASES KEPT WITHIN DESIGN LIMITS

13. HYDROGEN MONITORS STRATEGICALLY LOCATED

14. GASEOUS/LIQUID EFFLUENTS MONITORED

15. TRITIUM CONCENTRATED IN LESS RADIOLOGICALLY HAZARDOUS ELEMENTAL FORM, AND NOT IN THE OXIDE FORM

16. PURE TRITIUM IMMOBILIZED
ON A TITANIUM SPONGE

VERY STABLE
550 DEG C TO LIBERATE

II MINIMIZE HAZARDS THROUGH SOUND OPERATING PROGRAMS

1. STAFF SELECTION

   - SPECIFICALLY ASSIGNED OPERATING STAFF
   - DRAWN FROM OTHER NGD FACILITIES
   - SOME CHEMICAL PROCESS EXPERIENCE
   - SPECIFICALLY ASSIGNED TECHNICAL STAFF
   - SUPPORT STAFF

2. STAFF TRAINING

   2.1 OPERATING STAFF

   - 8 MONTH PROGRAM: SYSTEMS
     MICRO COMPUTER SIMULATION
     ADMINISTRATION
     RADIATION
     EMERGENCY

   2.2 MAINTENANCE STAFF

   - SPECIALIZED EQUIPMENT
   - FAMILIARIZATION AT FACILITIES USING SIMILAR EQUIPMENT

3. DOCUMENTATION

4. OPERATING PROGRAMS

   - ROUTINES
   - PREVENTATIVE MAINTENANCE CALL-UPS
   - SYSTEM TESTING

5. ACCESS AND WORK CONTROL

- NO SMOKING
- STRICT CONTROL HOT WORK
- NON-SPARKING CONTROL
- ACCESS RESTRICTED

6. QUALITY ASSURANCE

- OPERATION OF THE TRF IS IN ACCORDANCE WITH DNGS QUALITY ASSURANCE PROGRAM

III. DEAL WITH IMMEDIATE HAZARDS WHEN THEY ARISE

1. MONITORING

2. EMERGENCY RESPONSE TEAMS

3. PROCEDURES - PROCESS CONTROL
   - EMERGENCY
   - PROVINCIAL

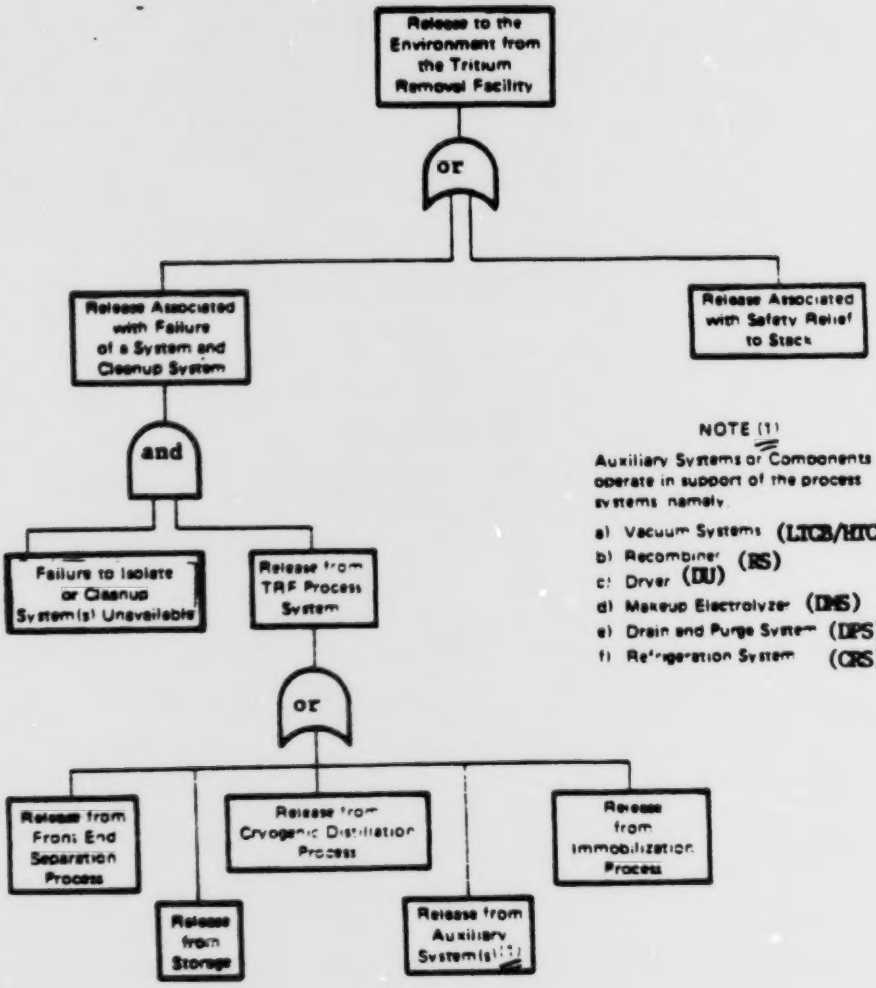

Release to the Environment from the Tritium Removal Facility
or
Release Associated with Failure of a System and Cleanup System
Release Associated with Safety Relief to Stack
and
Failure to Isolate or Cleanup System(s) Unavailable
Release from TRF Process System
or
Release from Front End Separation Process
Release from Storage
Release from Cryogenic Distillation Process
Release from Auxiliary System(s)[1]
Release from Immobilization Process
NOTE (1)
Auxiliary Systems or Components operate in support of the process systems namely
a) Vacuum Systems (LTCB/HTCB/CRSCB)
b) Recombiner (RS)
c) Dryer (DU)
d) Makeup Electrolyzer (DMS)
e) Drain and Purge System (DPS)
f) Refrigeration System (CRS)

FIGURE 3.1
Tritium Removal Facility Release Mechanisms

Summary of Dose and Release Rates from the D_2O Management Building at Darlington NGS 'A' After a Seismic Event Followed by Fire

Extreme Event Scenario - Case 3 (E3)

Time Period of Release	Type and Amount of Release (Ci)	Dose to Critical Individual at Exclusion Zone Boundary (914m) (mrem)
Short Term (0-1 hour)	34,400 - HTO 464,400 - T_2 T_2 gas oxidized to HTO by fire	305
Prolonged Release (1-25 hours)	825,500 - HTO	810
Long Term (25 hours to 4 days)	217,350 - HTO	135
	TOTAL:	1250

NOTES:

1. Adverse, unlikely climatic conditions.
2. No control actions are implemented for 4 days.
3. Catastrophic failure (severe seismic/or aircraft/or missile event - Destruction of TRF + HWMB) + Fire.
4. Max evaporation of HTO, DTO.
5. 100% oxidation T_2 —> HTO.
6. 200 m^3 released (34 Ci/kg DTO).
7. 3000 m^2 spill area.
8. Assumption - Airborne release only.

PR13

Radiological Consequences
Comparison Extreme Event vs
Moderate Event Scenario (Case M4)

I **Extreme Event**

Scenario	Climatic Conditions	Potential Dose (mrem)
E3	Adverse	1250

II **Moderate Event**

Scenario	Climatic Conditions	Potential Dose (mrem)
M4a - 20% of Releasable Inventory	Moderate Event Scenarios Pasquill D Wind Speed 5m/s	42
M4b - 50% of Releasable Inventory	"	87
M4c - 75% of Releasable Inventory	"	109
M4d - 75% of Releasable Inventory	Pasquill F Wind Speed 2m/s	168

PR13

PLASMA CENTRIFUGE FOR ZIRCONIUM SEPARATION

J.L. Hirshfield
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Science Based Industries Campus
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PO Box 3045
Jerusalem, Israel

Some of the work described here has also been reported in a paper presented at the XIIIth International Symposium on Discharges and Electrical Insulation in Vacuum, Paris, 1988: "Vacuum Arcs for Plasma Centrifuge Isotope Enrichment", J.L. Hirshfield, L.A. Levin and O. Danziga, to appear in the IEEE Transaction on Plasma Science. An earlier paper on this subject is "Vacuum Arc Plasma Centrifuge for Element and Isotope Separation". M. Geva et al, IEEE Transactions on Plasma Science, PS-15, 583-588 (1987).

PLASMA CENTRIFUGE FOR ZIRCONIUM SEPARATION

J. L. Hirshfield, L. A. Levin
and O. Danziger

Isomed Ltd., P.O.B. 23016
Jerusalem 91230, Israel

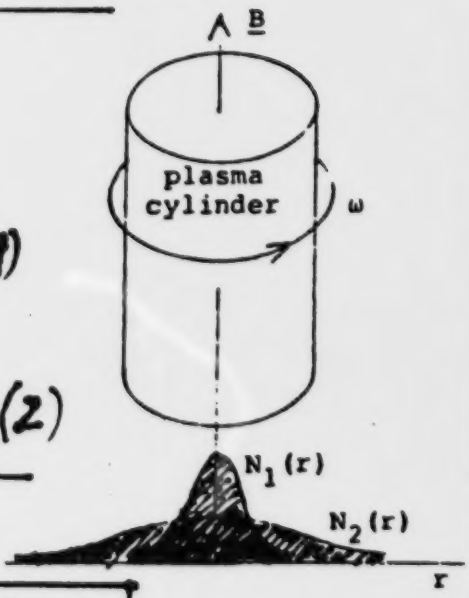
ISOMED

OUTLINE

- Review Plasma Centrifuge requirements for Isotope Separation
- DC vacuum arc of Vasin et al.
- Proposed mechanism for DC vacuum arc
- ISOMED experimental apparatus and results
- Conclusions

ISOMED

PLASMA CENTRIFUGE BASICS



Enrichment factor: $q(r) = \dfrac{N_2(r)/N_2(0)}{N_1(r)/N_1(0)}$ (1)

For two ion species: $q(r) = \exp\left(\dfrac{\omega^2 r^2 \Delta M}{2kT}\right)$ (2)

$\Delta M = M_2 - M_1$

Typical values: ω = 100,000 rad/sec,
ΔM = 2 amu, T = 1 eV, r = 7 cm.
Published measurement gives $q < 3$.

[M. Geva et al. IEEE Trans. on Plasma Science PS-15, 583 (1987)]

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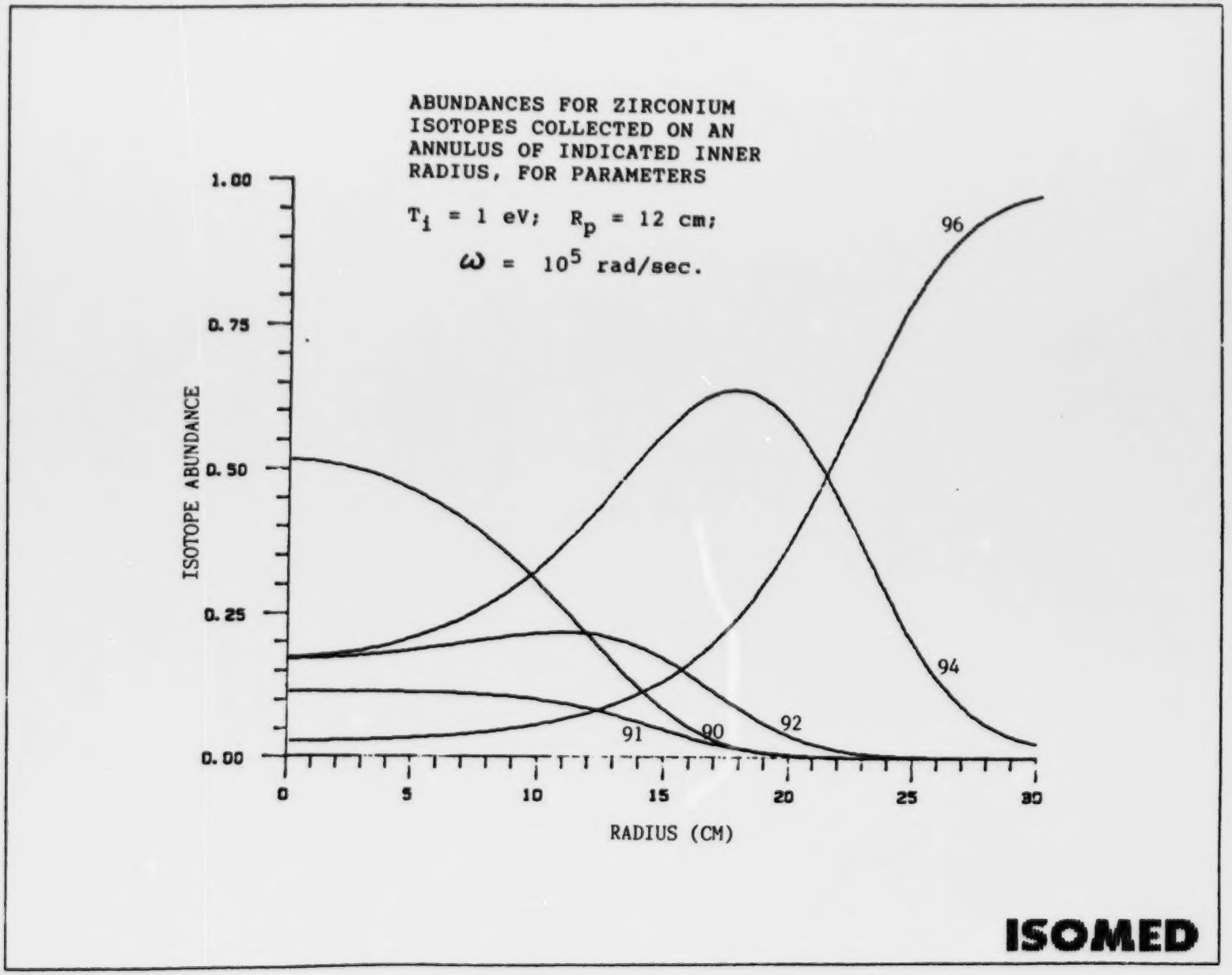
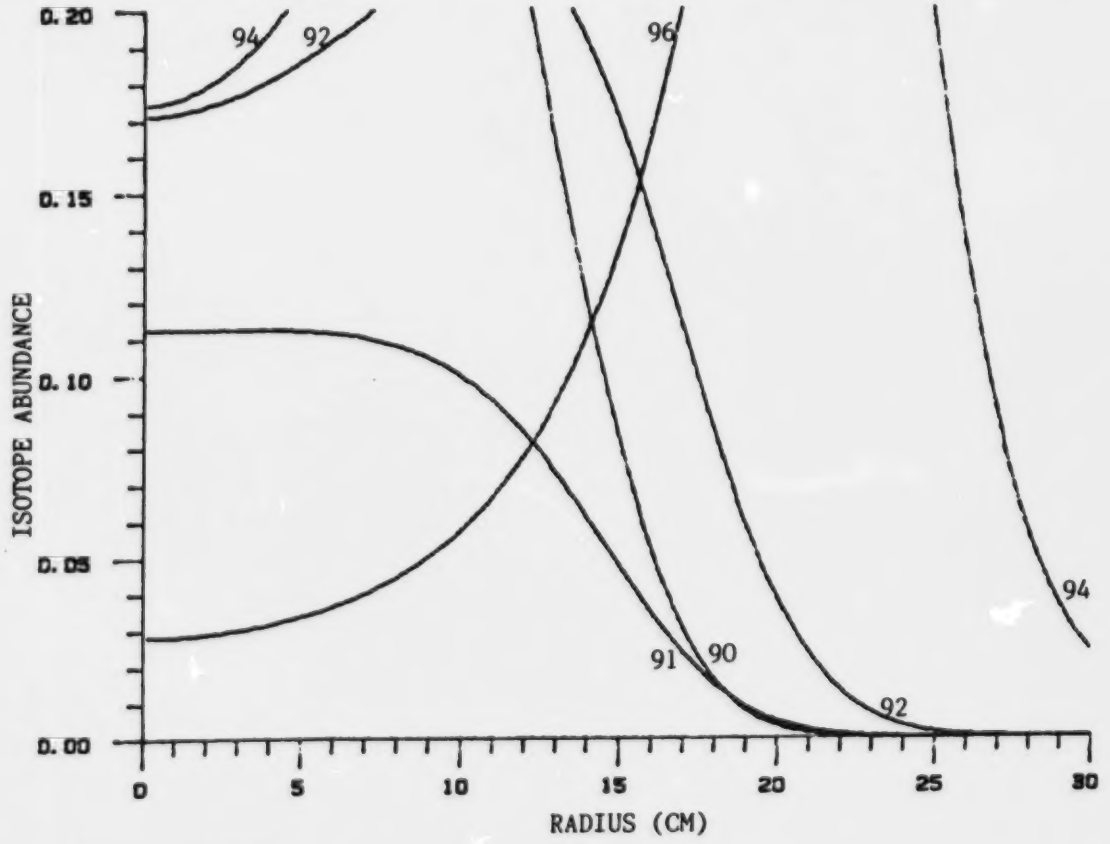

ABUNDANCES FOR ZIRCONIUM ISOTOPES COLLECTED ON AN ANNULUS OF INDICATED INNER RADIUS, FOR PARAMETERS
T_i = 1 eV; R_p = 12 cm;
ω = 10^5 rad/sec.
ISOTOPE ABUNDANCE
1.00
0.75
0.50
0.25
0.00
0
5
10
15
20
25
30
RADIUS (CM)
96
94
92
91
90
ISOMED



SAME AS PRIOR DIAGRAM,
EXCEPT THAT VERTICAL
SCALE IS EXPANDED

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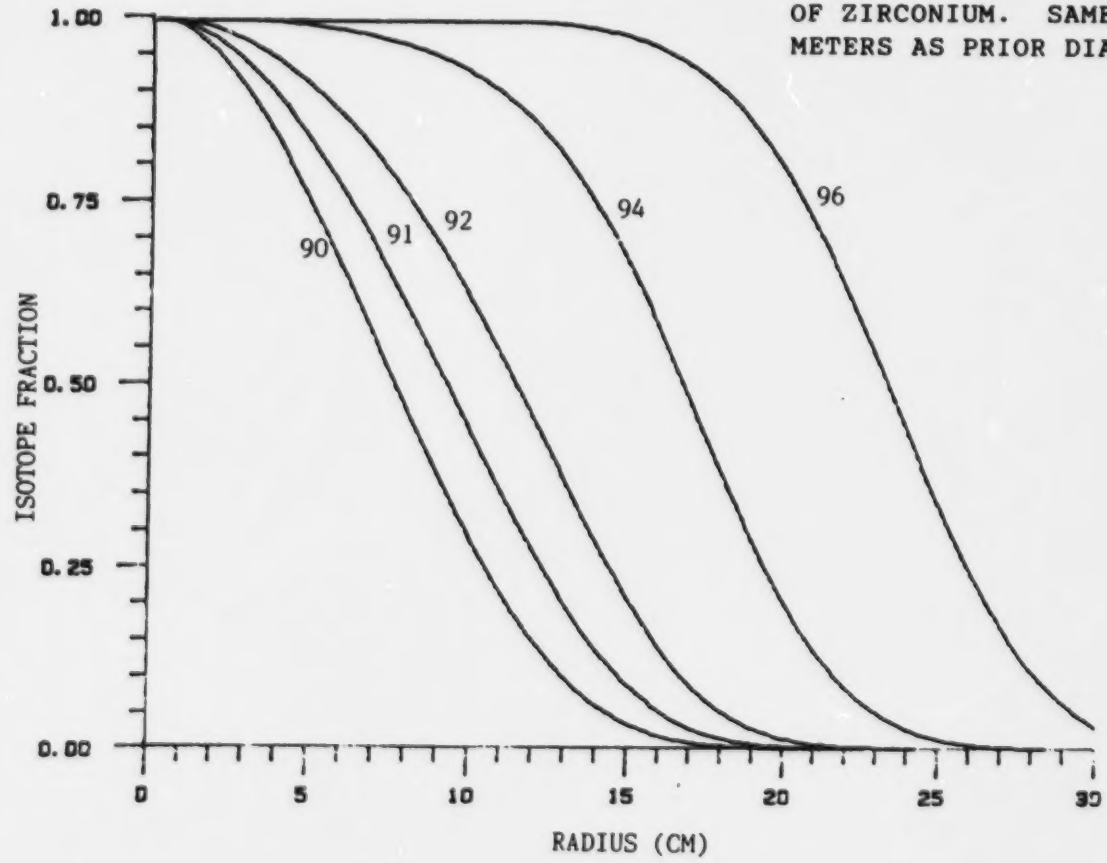
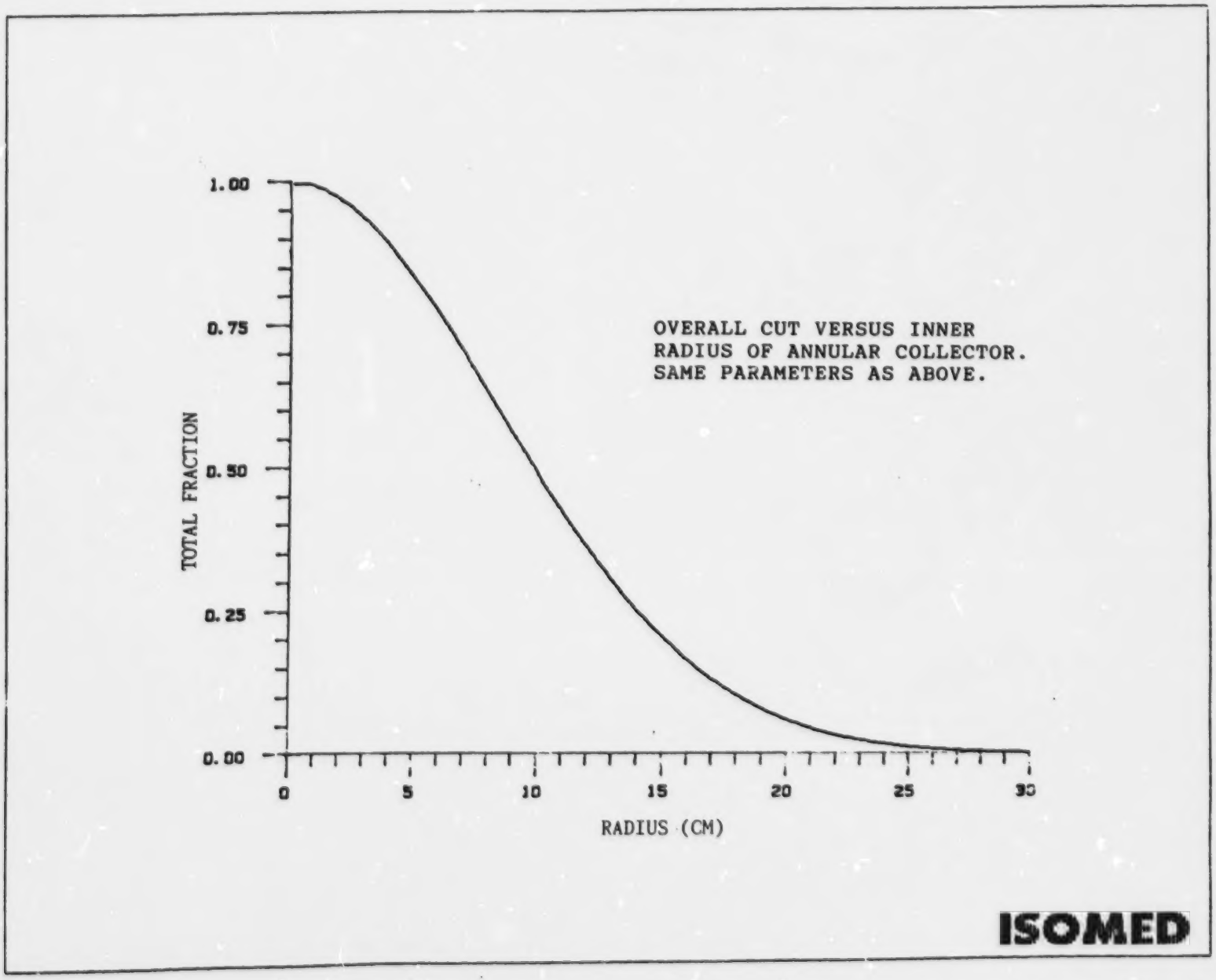


FRACTIONS COLLECTED ON AN ANNULUS OF INDICATED INNER RADIUS FOR THE FIVE ISOTOPES OF ZIRCONIUM. SAME PARAMETERS AS PRIOR DIAGRAMS.

ISOMED


1.00
0.75
0.50
0.25
0.00
TOTAL FRACTION
0
5
10
15
20
25
30
RADIUS (CM)
OVERALL CUT VERSUS INNER
RADIUS OF ANNULAR COLLECTOR.
SAME PARAMETERS AS ABOVE.
ISOMED

BASIC PLASMA PROPERTIES

- free streaming electrons tied to B-field lines
- frequent ion-ion collisions
- infrequent ion-neutral collisions
- small ion gyration radius
- axisymmetry
- high mass throughput (> 1 gm/minute)

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CONFIGURATION OF D. C. VACUUM ARC

A.I.Vasin, A.M.Dorodnov and V.A.Petrosov *

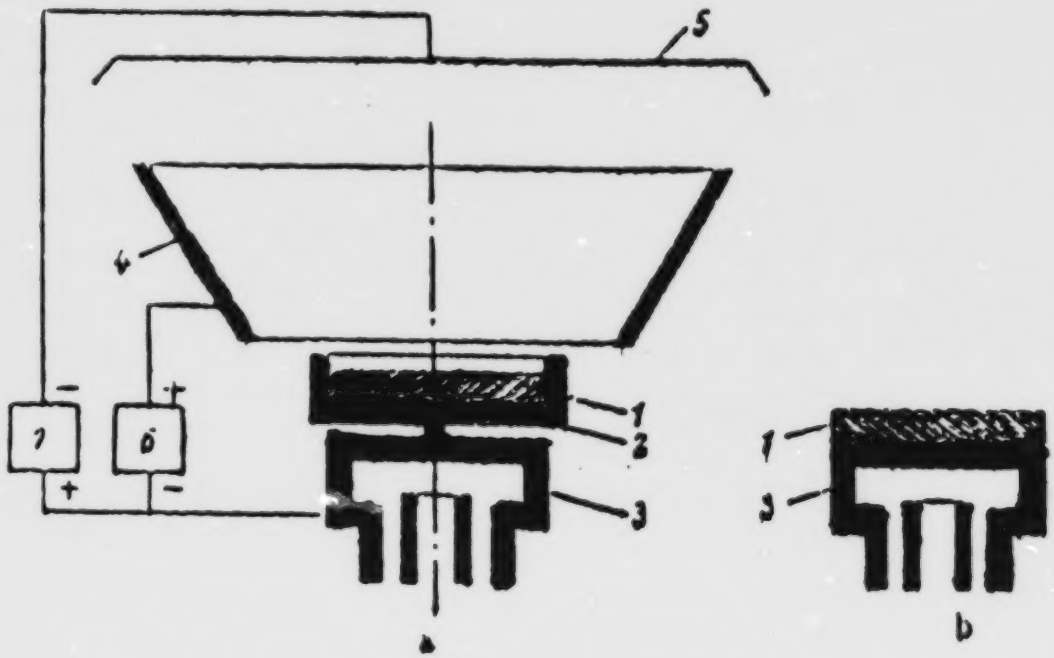
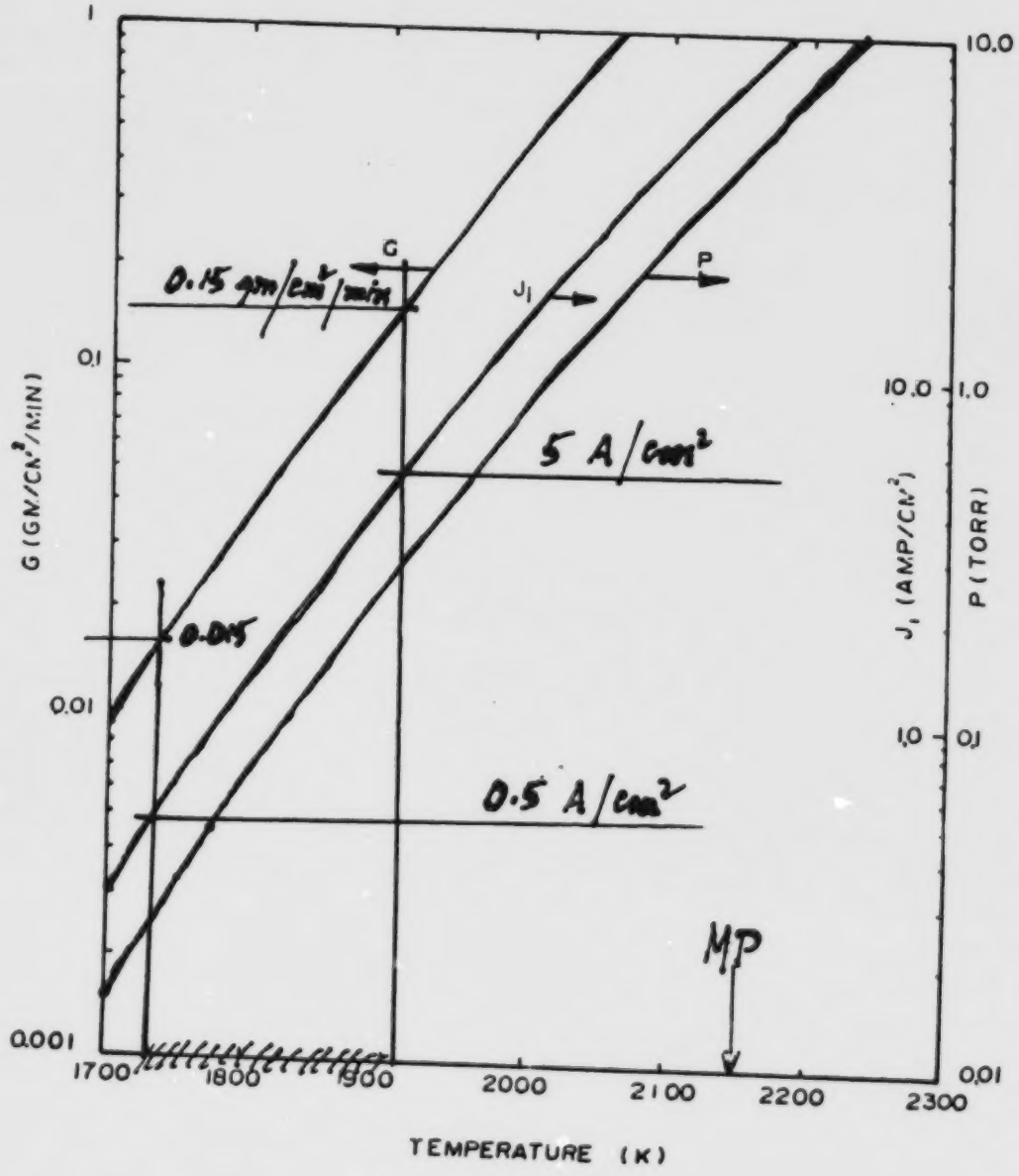


FIG. 1. The discharge apparatus. a: With "hot" cathode. b: With "cold" cathode. 1) Cathode of evaporating material; 2) crucible; 3) cooled holder; 4) anode; 5) Faraday cup; 6) discharge power supply; 7) voltage source for the Faraday cup.

634 * Sov. Tech. Phys. Lett. 5(12), December 1979

Chromium

Vapor pressure P ———
Mass evaporation rate G ———
Equivalent ion current density ———
(Z = 1, 100% ionization)



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VARIATIONS ON VDP CONFIGURATION

- external cathode/crucible heating and temperature control
- increased cathode diameter
- external axial magnetic field
- removal of the anode by an arbitrary distance along the magnetic field

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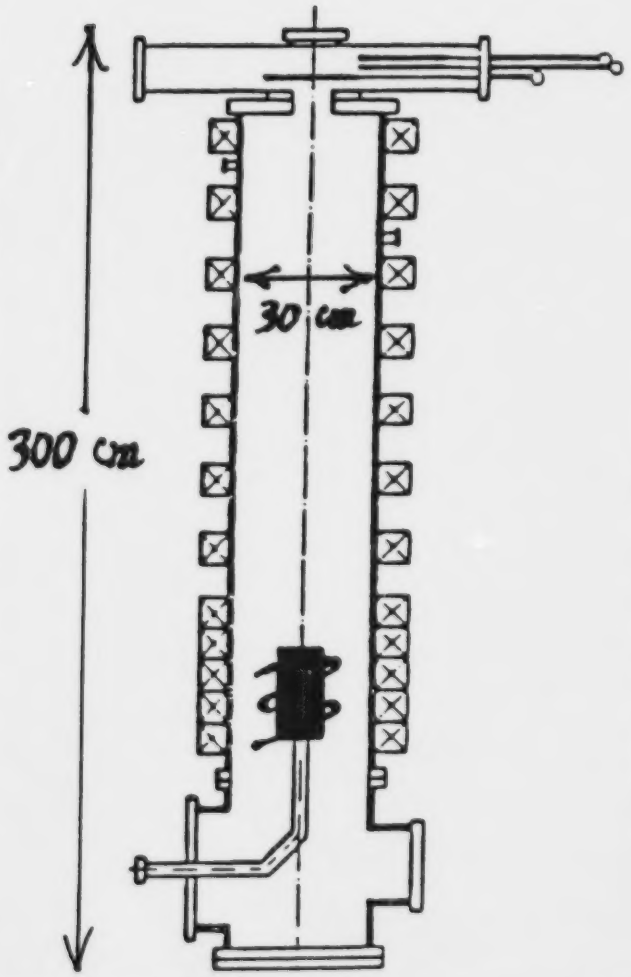
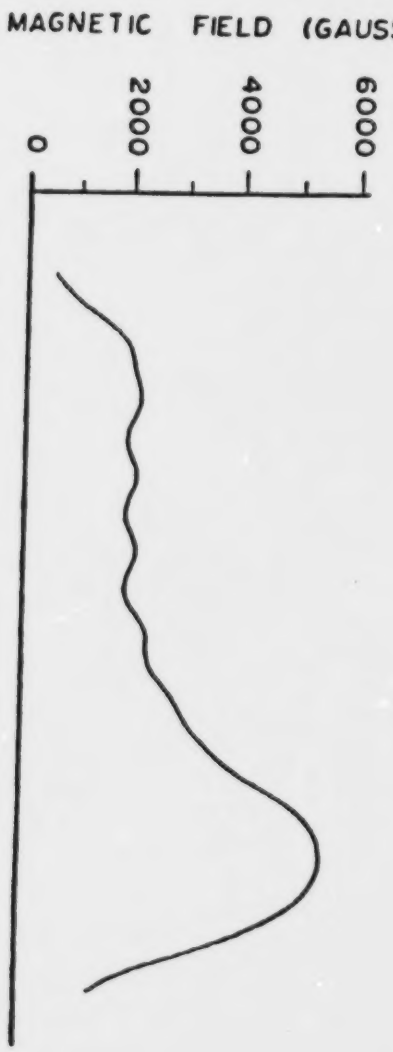
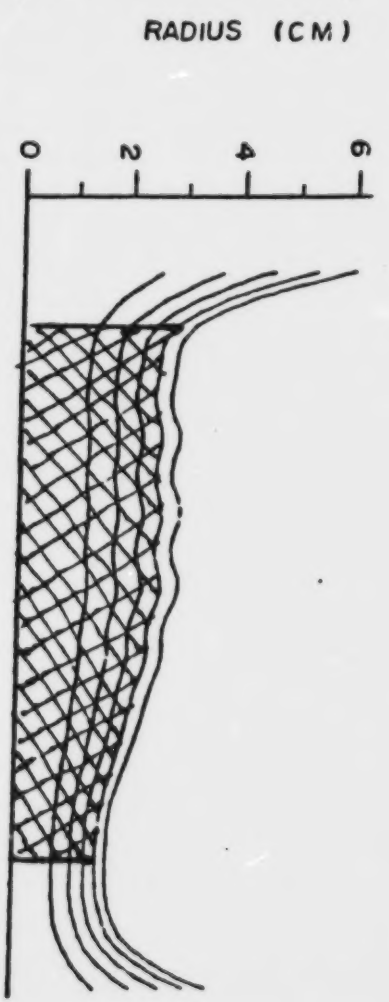
EXPERIMENTAL PLASMA CENTRIFUGE DEVICE







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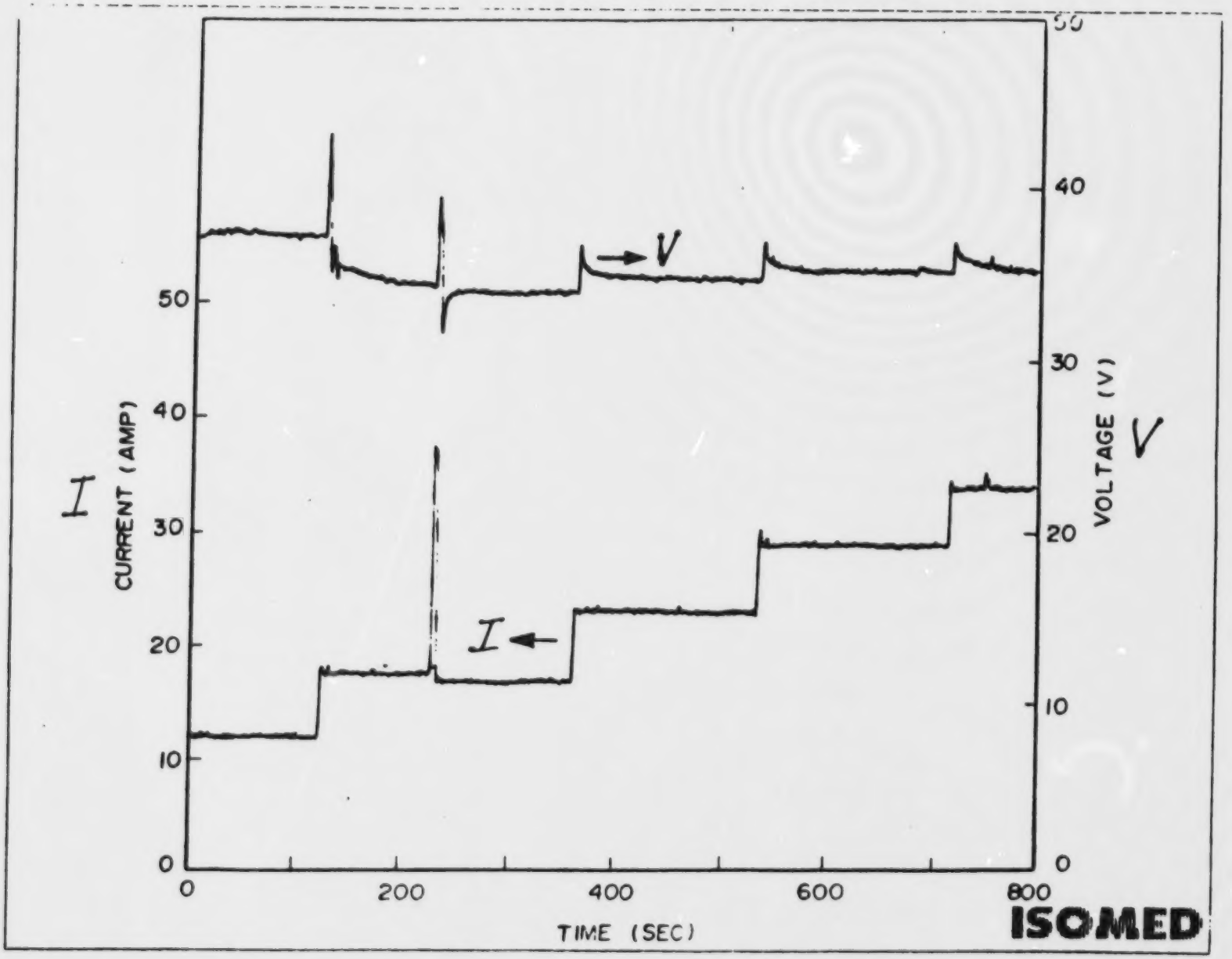

I
CURRENT (AMP)
0
10
20
30
40
50
V
VOLTAGE (V)
0
10
20
30
40
50
→V
I←
0
200
400
600
800
TIME (SEC)
ISOMED

89-49

LASER SEPARATION OF ZIRCONIUM ISOTOPES

H.D. Morrison
Ontario Hydro Research Division

P.A. Hackett, D.M. Rayner, and O.L. Bourne
National Research Council of Canada

At the Second Isotope Separation Workshop, Peter Hackett and Orson Bourne presented talks on zirconium AVLIS. They demonstrated its scientific feasibility and expressed the need to continue investigations to put limits on the feasibility. To that end, Ontario Hydro and NRC collaborated on some research into AVLIS of zirconium. We examined the spectroscopy of zirconium to determine paths to ionization from the ground state accessible with copper vapour laser pumped dye lasers. We also demonstrated isotopic selective excitation on one such path with a new single mode dye laser developed by NRC and Lumonics. In this paper we report on hyperfine and isotope shifts in zirconium and discuss their implications for AVLIS. For more experimental details see "Pulsed single mode laser ionization of hyperfine levels of zirconium-91" by P.A. Hackett, H.D. Morrison, O.L. Bourne, B. Simard and D.M. Rayner, to be published in the December 1988 issue of the Journal of the Optical Society of America, series B.

Slide 2 shows the reduction in thermal neutron absorption cross-section of zirconium that can be achieved by reducing the concentration of one isotope, ^{91}Zr. With ^{91}Zr at the 3% level the cross-section is less than half its original value. Reduction to 6.5%, however, is sufficient to allow a 50% increase in wall thickness of pressure and calandria tubes in CANDU reactors without increasing neutron absorption.

One method for depleting the concentration of ^{91}Zr is atomic vapour laser isotope separation (AVLIS) developed by Lawrence Livermore Laboratories for the separation of uranium. Of the three main process stages in AVLIS, this paper will only examine the middle one shown in Slide 3, which is isotope selective ionization by photons. We will show that the feasibility of zirconium AVLIS relies on exploiting the hyperfine shifts of ^{91}Zr rather than the isotope shifts.

A three-step excitation scheme from the ground state of zirconium to the ionization potential, depicted in Slide 4, requires photons with an average wavelength of 560 nm. Within 1300 cm^{-1} of the ground state lie two metastable levels. In an atomic beam all three levels will be populated, so that as many as three separate wavelengths will be needed in the first excitation step to achieve the desired depletion of ^{91}Zr. The total number of wavelengths can be minimized by requiring that the first step transitions have a common upper level.

The table in Slide 5 lists the four excited states that are accessible by copper vapour laser pumped dye lasers from at least two of the ground states. We examined five of the transitions to these excited states with high resolution laser induced fluorescence to assess their utility for isotope separation. The spectrum of the 613.6 nm transition in Slide 6 reveals peaks for the even isotopes with heights corresponding approximately to their natural abundance and spread over 500 MHz. The ^{91}Zr appears in five peaks arising from 13 hyperfine transitions. Analysis of this spectrum shows that the hyperfine constants for the $^3F_2$ excited state are close to zero. This spectrum clearly illustrates the two alternatives for isotope separation: ionize the even isotopes to enrich the ions or ionize the ^{91}Zr to deplete the atomic beam. The 613.6 nm transition is only useful for ionizing the even isotopes.

From the spectra we derived the hyperfine structure constants listed in Slide 9 for the four excited states of interest. Then we calculated the spectrum for all the transitions to these levels to assess their utility for isotope separation. Our conclusions are summarized in Slide 10: the most promising transitions for ^{91}Zr excitation are to the $^3F_3$ and $^3D_3$ levels. The next step in finding a useful excitation scheme is to find resonant transitions from these levels up to the ionization potential. Slide 11 illustrates the intermediate levels discovered from three of the first excited levels, and lists maximum wavelengths for the ionization step.

To demonstrate selective ionization of ^{91}Zr we chose the 593.7 nm transition with subsequent ionization by two photons at 544.5 nm. Slide 12 shows a representation of the spectrum at 593.7 nm with labels on the hyperfine transitions labelled corresponding to their hyperfine quantum numbers in the ground state (9 for 9/2, 7 for 7/2, and so on). To access all the ^{91}Zr in the ground state, we must excite at least one transition from each of the hyperfine levels. This can be accomplished by using a single laser with a bandwidth of about 500 MHz tuned to the high frequency edge of the 593.7 nm spectrum. A specially built single mode dye laser was applied to this task and mass spectra of the ions were recorded as this laser was tuned across the transition. The results appear in Slide 13. The selectivity for ^{91}Zr shown in Slide 14 was calculated from the mass spectra. Clearly, the selectivity is higher than 10 on both edges of the spectrum.

A simple model of the AVLIS process, shown in Slide 15, examines the stripping efficiency required to achieve certain levels of ^{91}Zr depletion. The stripping efficiency is a product of the fraction of zirconium atoms in levels available for ionization, the fraction of these that are ionized, and the fraction of ions that are collected. To deplete ^{91}Zr to 3% requires an efficiency of 80%, with a minimum selectivity of 5. Slide 16 summarizes the dependence of the fraction available for ionization as a function of the electronic temperature of the zirconium energy levels. Obviously, to achieve a high stripping efficiency the electronic temperature in the atomic beam must be colder than the kinetic temperature required to vaporize the atoms.

Finally, Slide 17 lists the laser energy required to produce denatured zirconium calculated with the simple model mentioned above. Actual dollar costs can be estimated by assuming a value for laser energy of about $100/MJ. As the laser costs may well dominate the AVLIS process, we predict that denatured zirconium would cost less than $1000/kg for 3% ^{91}Zr produced by excitation of ^{91}Zr.

In conclusion, the feasibility for producing zirconium depleted in ^{91}Zr by AVLIS has been demonstrated by this and previous work. Possible excitation schemes have been identified and selectivity has been measured. The estimated product costs lie well below the added values estimated for using denatured zirconium in pressure tubes in CANDU reactors ($3000/kg). Thus, it is worthwhile to pursue the development of Zr AVLIS and continue to refine our estimates of the costs.

LASER SEPARATION of ZIRCONIUM ISOTOPES

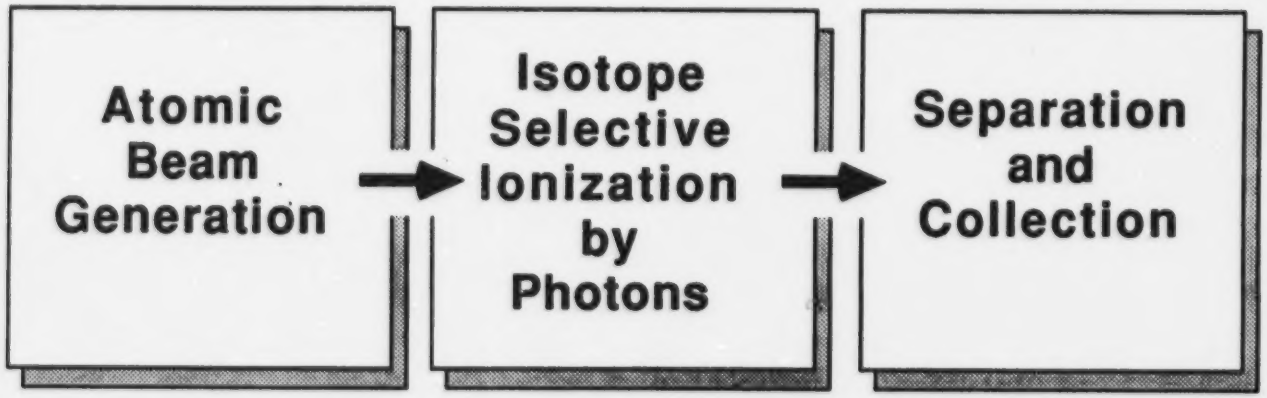
Hugh Morrison — ONTARIO HYDRO

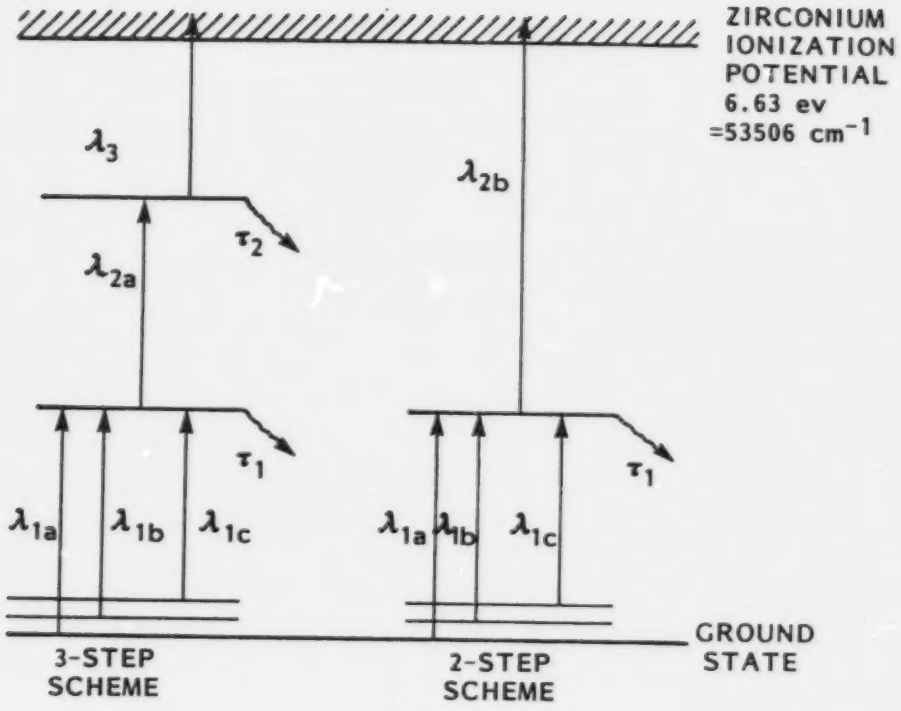
Peter Hackett, David Rayner, Orson Bourne — NATIONAL RESEARCH COUNCIL OF CANADA

ZIRCONIUM ISOTOPE ABUNDANCES AND NEUTRON CROSS-SECTIONS

Mass Number	Natural Abundance (%)	Thermal Neutron Absorption Cross-Section (mb)
90	51.46	14.4
91	11.23	1360
92	17.11	180
94	17.40	50
96	2.80	21
Natural Zirconium		200
Zirconium (3% 91)		93

Atomic Vapour Laser Isotope Separation

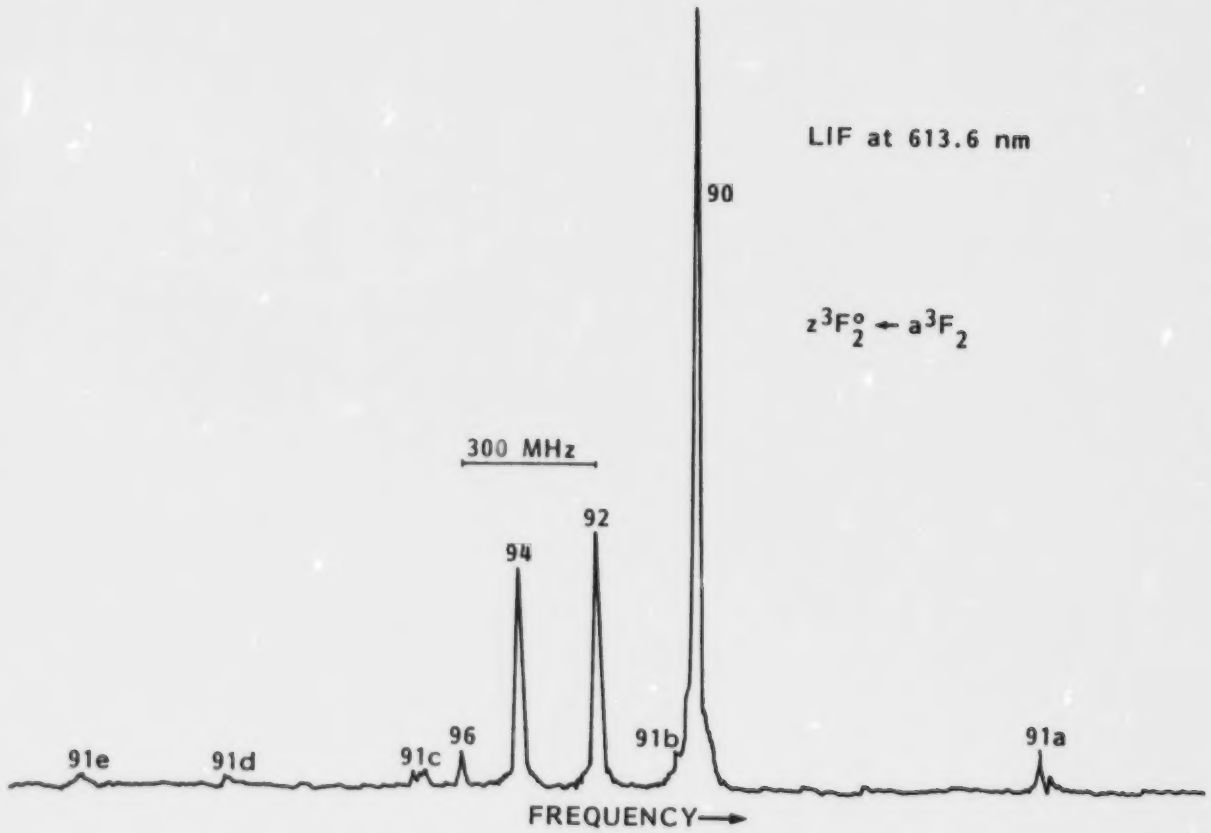



ZIRCONIUM
IONIZATION
POTENTIAL
6.63 ev
=53506 cm⁻¹
λ3
λ2b
τ2
λ2a
τ1
τ1
λ1a
λ1b
λ1c
λ1a
λ1b
λ1c
GROUND
STATE
3-STEP
SCHEME
2-STEP
SCHEME

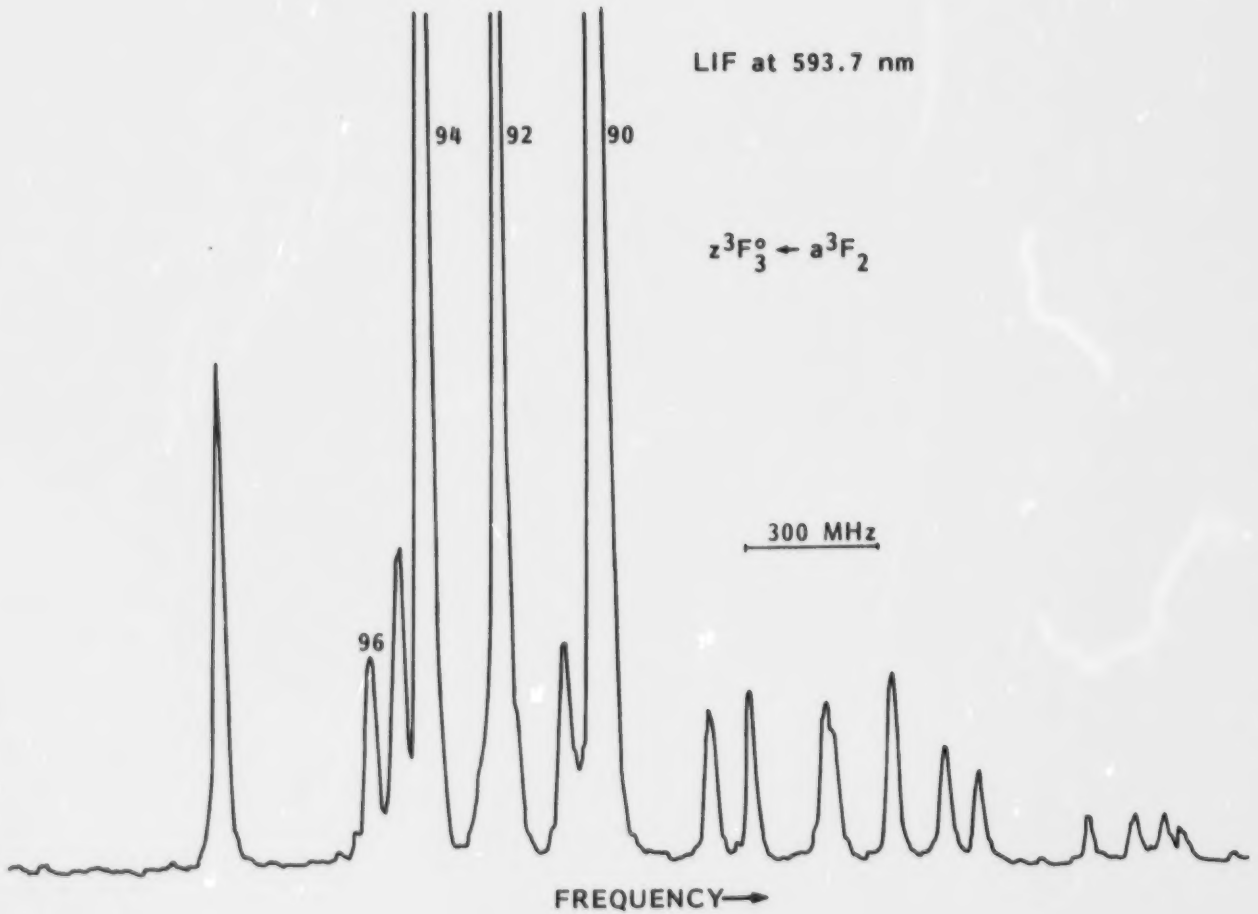
ZIRCONIUM TRANSITIONS (nm) ACCESSIBLE TO COPPER VAPOUR PUMPED DYE LASERS

Excited State	Ground States: ^3F_J J=2	J=3	J=4
$^3F_2$	*613.6	635.9	---
$^3F_3$	*593.7	*614.5	640.9
$^3D_2$	561.4	*579.9	---
$^3D_3$	548.1	565.8	*588.1

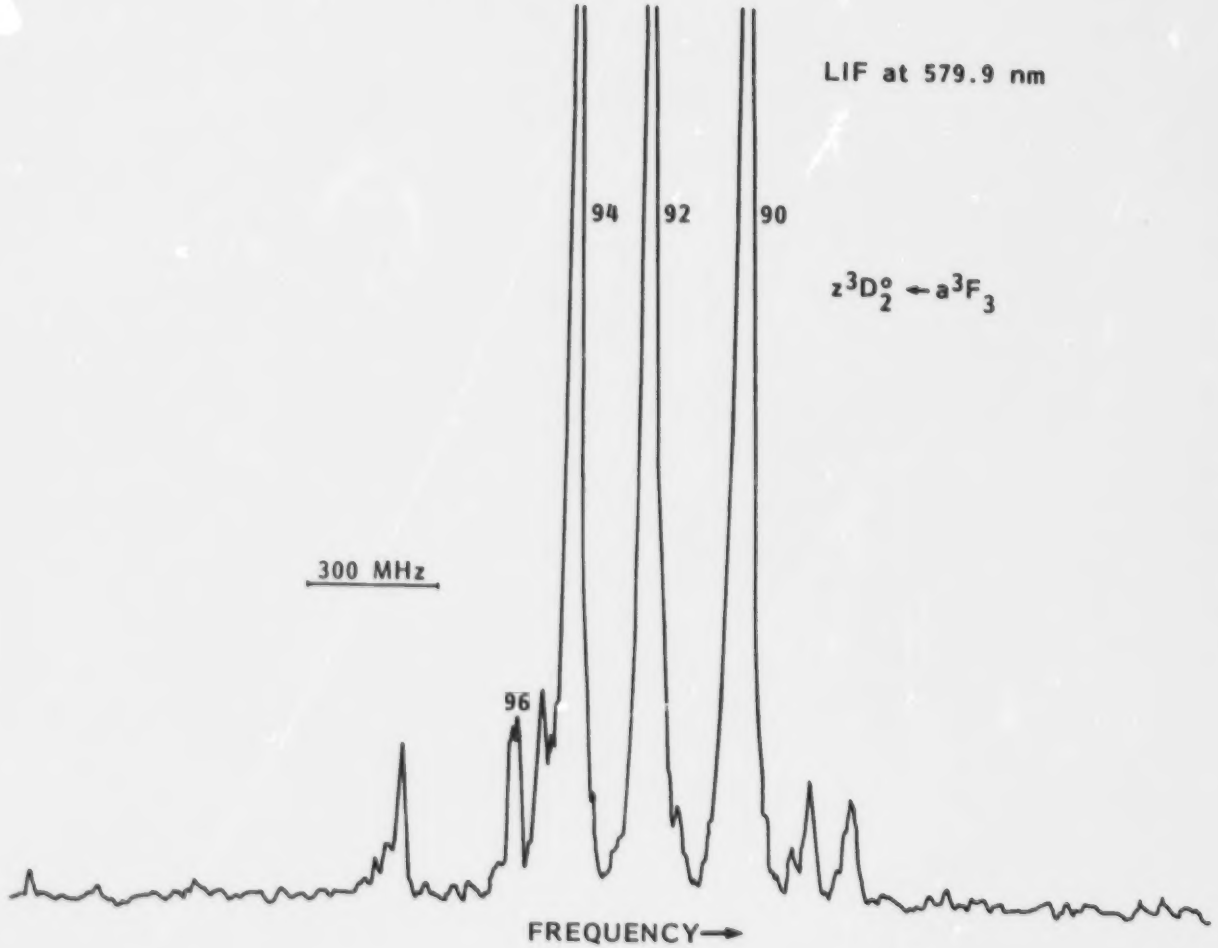
* Examined by High Resolution Laser Induced Fluorescence


LIF at 613.6 nm
90
$z^3F_2^o \leftarrow a^3F_2$
300 MHz
92
94
91e
91d
91c
96
91b
91a
FREQUENCY→

89-49


LIF at 593.7 nm
94
92
90
$z^3F^o_3 \leftarrow a^3F_2$
300 MHz
96
FREQUENCY→

89-49


LIF at 579.9 nm
94
92
90
$z^3D^o_2 \leftarrow a^3F_3$
300 MHz
96
FREQUENCY→

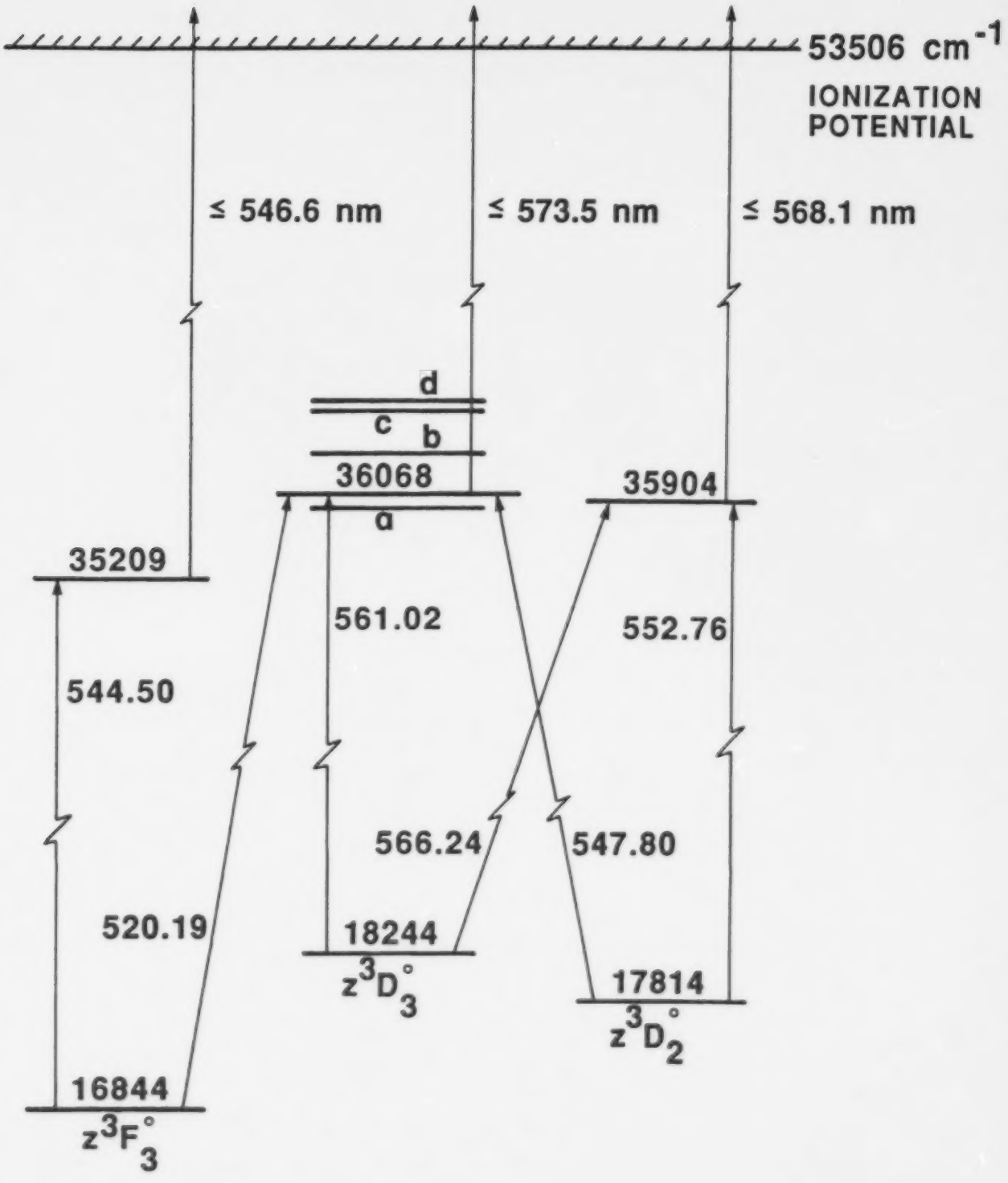
^{91}Zr HYPERFINE STRUCTURE CONSTANTS

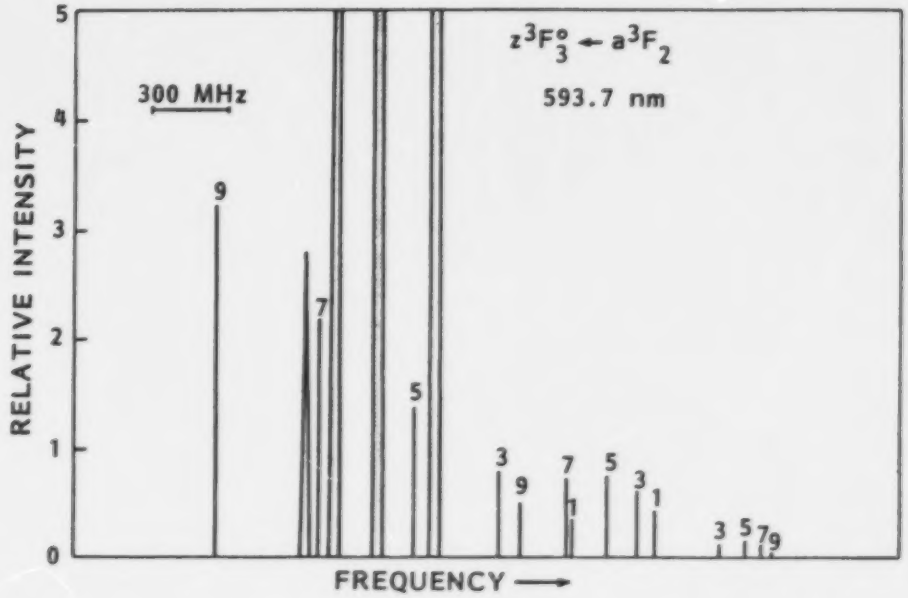
Excited State	Dipole, A (MHz)	Quadrupole, B (MHz)
$^3F_2$	-5(1)	0(10)
$^3F_3$	-211.0(29)	17(14)
$^3D_2$	-180(10)	20(20)
$^3D_3$	-301.8(3)	-24(8)

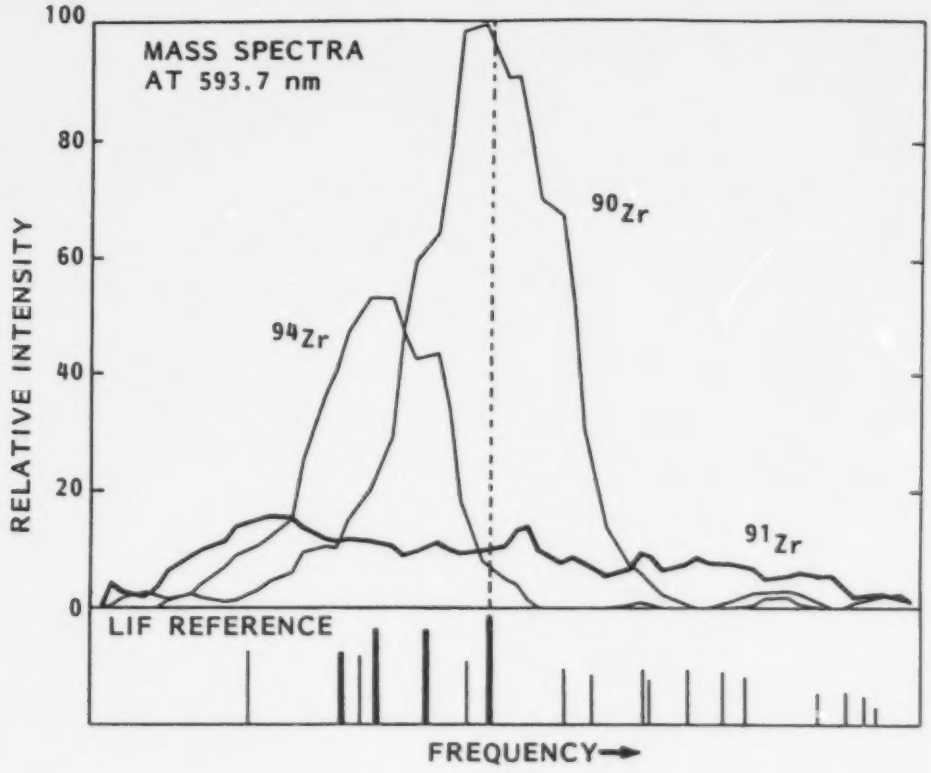
ZIRCONIUM TRANSITIONS (nm) ACCESSIBLE TO COPPER VAPOUR PUMPED DYE LASERS

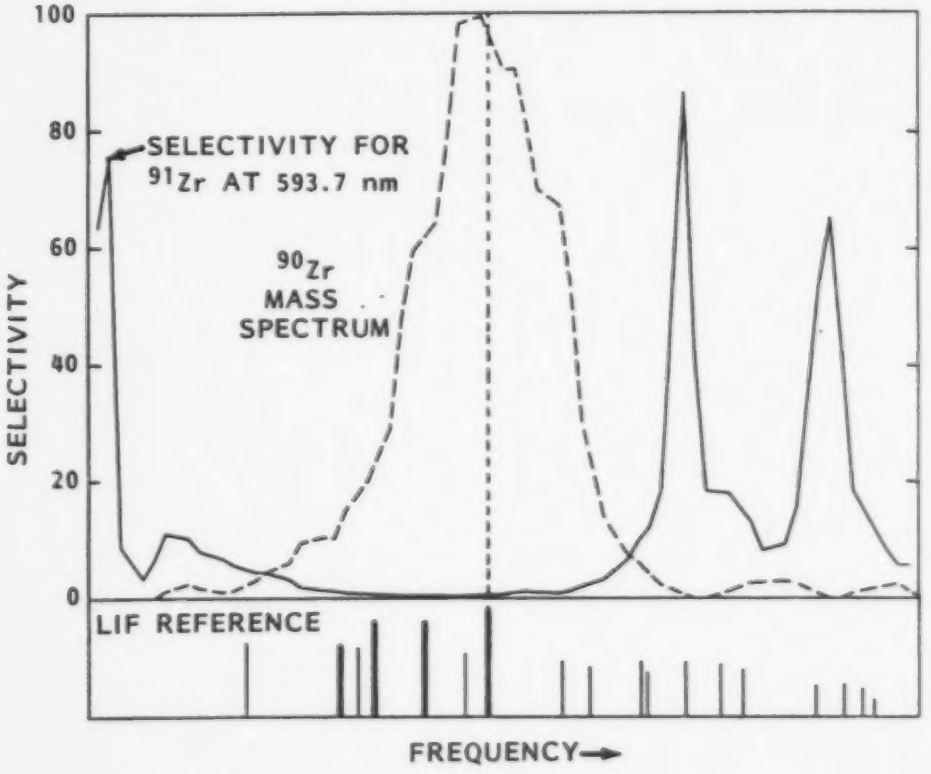
and Suitable for Isotope Selective Excitation

	Excited State	Ground States: ^3F_J J=2	J=3	J=4
Even	$^3F_2$	613.6	~~635.9~~	---
^{91}Zr	$^3F_3$	593.7	614.5	640.9
^{91}Zr	$^3D_2$	561.4	~~579.9~~	---
^{91}Zr	$^3D_3$	548.1	565.8	588.1


53506 cm-1
IONIZATION POTENTIAL
≤ 546.6 nm
≤ 573.5 nm
≤ 568.1 nm
d
c
b
a
36068
35904
35209
561.02
552.76
544.50
566.24
547.80
520.19
18244
z3D°3
17814
z3D°2
16844
z3F°3


$z^3F^o_3 \leftarrow a^3F_2$
593.7 nm
300 MHz
RELATIVE INTENSITY
FREQUENCY
0
1
2
3
4
5
9
7
5
3
9
7
1
5
3
1
3
5
7
9


MASS SPECTRA
AT 593.7 nm
RELATIVE INTENSITY
100
80
60
40
20
0
^{90}Zr
^{94}Zr
^{91}Zr
LIF REFERENCE
FREQUENCY→


SELECTIVITY
100
80
60
40
20
0
SELECTIVITY FOR
^{91}Zr AT 593.7 nm
^{90}Zr
MASS
SPECTRUM
LIF REFERENCE
FREQUENCY→

Modelling AVLIS of Zr

Stripping Efficiency

$$\eta = f_a \times f_i \times f_c$$

Available

Ionized

Collected

Need :

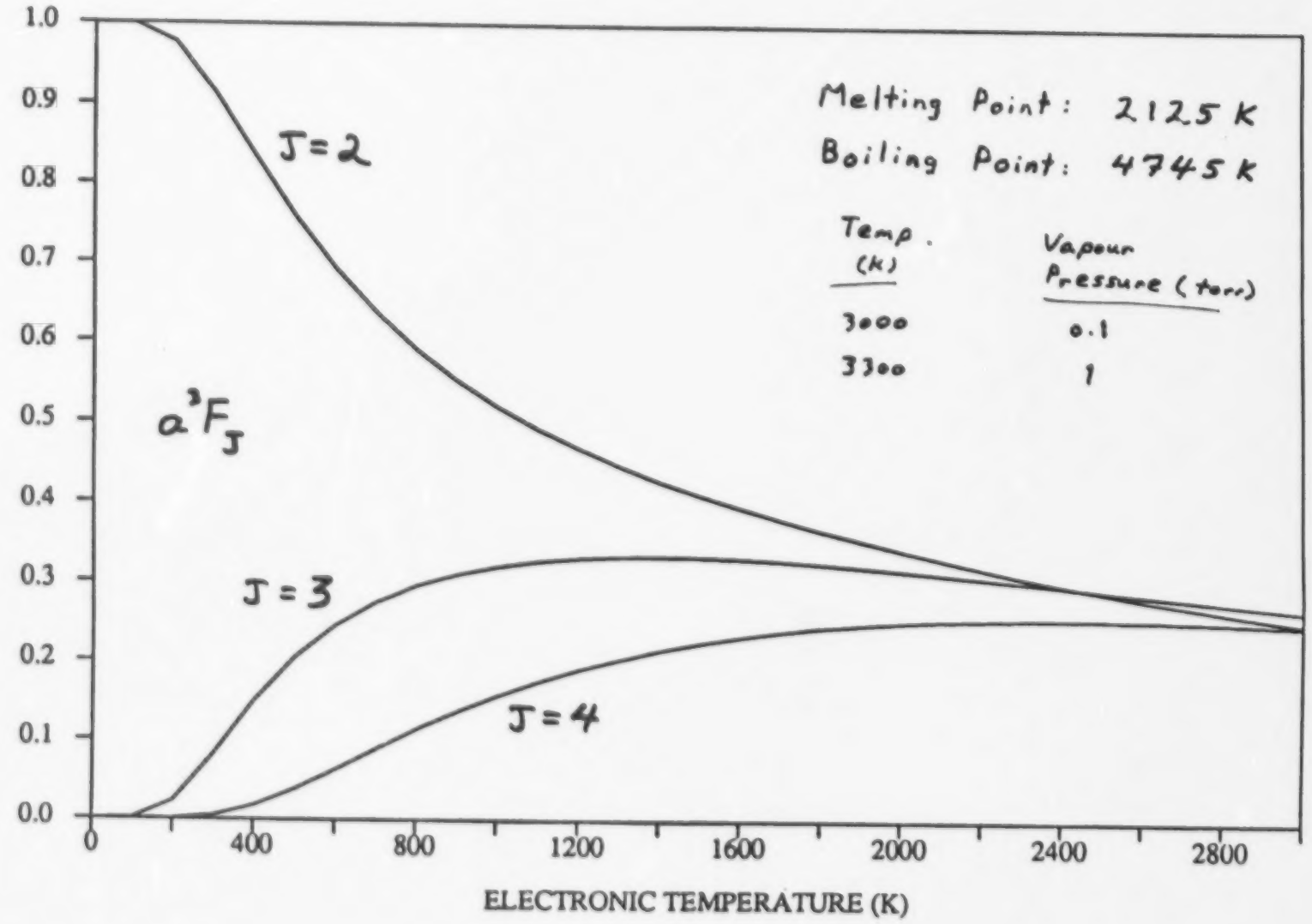
$\eta_{91} \geq 0.5$ 6.5% Zr-91

$\eta_{91} \geq 0.8$ 3.0% Zr-91

Selectivity : $S \equiv \eta_{91} / \eta_{even}$

$S_{min} \geq 5$

ZIRCONIUM LEVEL POPULATIONS



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LASER ENERGY REQUIREMENTS

Isotope Photo-Ionized	Product (%^{91}Zr)	Laser Energy (MJ/kg-Product)
^{91} Zr	6.5	3.8
^{91} Zr	3	6.5
All Even	6.5	16.8
All Even	3	29.2

Assumptions :

Isotope Selectivity = 10
Photon Utilization = 20%
Ion Collection Efficiency = 100%

ZIRCONIUM: SPECIFICATIONS, INFLUENCE OF IMPURITIES ON PROPERTIES, IMPURITY REMOVAL AND ANALYSIS

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Albany, OR 97321

INTRODUCTION

Specifications of nuclear grade zirconium, and thus the processes used to produce it, have been refined over the interval in which the material has been in service. The purpose of this paper is to recapitulate compositional specifications and the effects of the more important impurities and alloying additions, to describe briefly how the impurity concentrations are reduced to acceptable levels, and to outline how the product is analyzed to verify conformance with compositional specifications.

SPECIFICATIONS

Zirconium 2.5% Nb ingot compositional specifications are recited in Table 1, for ASTM 350, for a Canadian manufacturer of pressure-tubes, and for several other users, where other impurities are mentioned, or where limits are sharply different. This list thus gives the elements whose effects are, or have been, considered a concern, and the maximum tolerable levels thereof.

INFLUENCE OF IMPURITIES ON PROPERTIES

Impurities that affect properties of concern are given in Sheet 1. Nuclear properties, or more properly those properties of an impurity that could interfere with the operation of fission reactor, clearly include a large capture cross-section for thermal neutrons and the capability to undergo fission. Impurities that influence yield strength, ultimate strength, and elongation at rupture are of interest from the standpoint of structural engineering. Regarding corrosion, impurities that accelerate the degradation of zirconium alloys in water or steam at reactor operating temperature are of primary concern.

Mechanical Properties

Table 2 gives a sampling of the effects of several additives and impurities on the yield stress, ultimate tensile stress and elongation at failure at room temperature and at 316C (600F) for zircalloy 2. Clearly, phosphorus has the most spectacularly undesirable effect, while oxygen and carbon cause strengthening at room temperature, at the expense of some ductility, and tin is a modest strengthener. These effects result variously from formation of solid solutions (Sn, O), formation and precipitation of intragranular phases (C, Fe+Cr), grain refinement (Si and C) and precipitation of second phases resulting in weakening of grain-boundaries (P).

Corrosion Properties

Effects of impurities and additives on corrosion behavior are grouped in Sheet 2. The strongly deleterious effects of

nitrogen and of carbon are illustrated in Figures 1a and 1b. In the concentration-range covered, nitrogen is present as a solute while carbon is present mostly as ZrC precipitates. These effects were a cause for concern in early attempts to use zirconium alloys in reactors.

Figure 2a shows the effect of tin addition on the corrosion resistance of pure zirconium, and Figure 2b shows the effect of tin on corrosion of zirconium containing 60 ppm N. In the latter case, tin additions result in improved corrosion resistance, while in the former, any addition of tin is deleterious. These findings lead to development of the zircalloys which are based on zirconium-tin alloys, tin being present to suppress the effects of nitrogen and of carbon. Figures 3a and 3b show the effect of nitrogen and carbon addition on the corrosion resistance of zircalloy 2; comparison with Figures 1a and 1b indicates that tin strongly diminishes the deleterious effects of these impurities. In addition, Figure 3a illustrates the phenomenon of break-away, that is, the exposure-time at which the corrosion rate changes from an approximately parabolic or cubic dependence on time to a linear dependence. In the case of nitrogen, the effect of increase in concentration is to diminish the time interval before onset of break-away. Other solutes have a similar effect and, like nitrogen, are avoided for this reason.

The effect of oxygen on zircalloy corrosion is not serious, as is shown in Figure 4. This is felicitous in view of the considerable strengthening effect of solute oxygen, particularly at lower temperatures.

Niobium is added to zirconium, as in the Zr-2.5%Nb alloy, largely because of its strengthening effect, which is accepted at a cost of decreased corrosion resistance relative to the zircalloys. The undesirable corrosion effects of niobium are more pronounced at levels below the solubility limit, 200 to 5000 ppm, than at the 2.5% level of the alloy in use. Corrosion resistance of this alloy is quite sensitive to heat treatment, as illustrated in Figure 5.

Small quantities of iron and chromium are added to the zircalloys, and additionally of nickel to zircalloy-2, to improve corrosion resistance further. Recent work has shown that the corrosion performance of the zircalloys can be improved considerably by adjusting the composition within the range of the existing specification. As in Zr-2.5 Nb, corrosion resistance of zircalloys is sensitive to heat treatment. Impurities such as titanium, copper, silver, germanium and lead accelerate corrosion of zirconium alloys. Careful experiments have not revealed any effect of aluminum in the range of 30-80 ppm. Reduction of the concentration of iron, chromium and nickel in zircalloys increases propensity to non-uniform, or nodular, corrosion for certain heat-treatments of zircalloys. Nodular corrosion

propensity in the break-away range is increased for zircalloys by increased levels of carbon, silicon, tin and especially phosphorus.

The effects of cobalt are similar to those of Fe & Ni, however, cobalt is objectionable on ground of nuclear properties, as is manganese, the effects of which on corrosion are, however, slight.

The effects of antimony on corrosion resistance of zirconium are similar to those of tin; however, addition of germanium to zirconium-antimony alloys raises their corrosion resistance to a level comparable to that of the zircalloys.

PRODUCTION OF ZIRCONIUM

Raw Material

The raw material from which most zirconium is produced is the mineral zircon, zirconium orthosilicate, $ZrSiO_4$. This occurs widely in the earth's crust, in a variety of igneous rocks and in the products of their break-down by weathering and other natural processes. Almost all commercially worked zircon deposits are present on beaches, where wave action has concentrated zircon along with other minerals of similar density and resistance to weathering and attrition. A range of ore-dressing techniques is used to separate zircon from these minerals, among which are rutile, ilmenite, corundum, monazite and xenotime. Specifications for zircon intended for manufacture of zirconium are given in Table 3; since the majority of the objectionable impurities occur in other minerals, their removal depends on the effectiveness of the ore-dressing. Some impurities, such as phosphorous, uranium and thorium are present substitutionally in the zircon lattice, and must be removed during subsequent processing. The levels of these impurities vary between zircons from different deposits and may be controlled by selection of the source. Fortunately, a small fraction of the total zircon mined is used for production of metal, and the impurities of concern in this application are often unimportant in other uses.

Purification

The process used at TWCA to produce zirconium from zircon is shown in Figure 6. Zircon is ground with petroleum coke then chlorinated at about 1100C in a fluidized-bed reactor to produce zirconium and silicon tetrachlorides. These are condensed separately and the zirconium tetrachloride dissolved in water to produce zirconium oxychloride solution. This solution is treated to remove iron, then mixed with ammonium thiocyanate solution to form zirconium and hafnium complexes and treated with ammonia to adjust the acidity. The solution is introduced to a counter-current, liquid-liquid extraction plant where hafnium and some

other impurities are removed from zirconium. The aqueous solution is treated to precipitate zirconium as sulfate and leave other impurities in solution. The zirconium sulfate is collected by filtration, converted to oxide with ammonia solution, then calcined to produce anhydrous zirconium oxide. The oxide is mixed with petroleum coke and chlorinated to produce pure zirconium tetrachloride, which is often sublimed to reject other impurities. The zirconium tetrachloride is then reduced to metal with magnesium, and the resulting magnesium chloride is separated to yield zirconium sponge. The sponge is crushed and graded, compacted along with alloying additives into cakes which are welded together and arc melted several times to produce zirconium ingots for subsequent fabrication.

Impurity removal starts in chlorination, where zirconium is separated from elements the chlorides of which have sharply different volatilities from zirconium tetrachloride, as shown in Sheet 3. Elements that accompany zirconium through the chlorination process are those that form chlorides of roughly similar volatility to zirconium tetrachloride, for example uranium and to a lesser extent, titanium, silicon and iron, and phosphorus, the pentachloride and oxychloride of which form stable addition compounds with zirconium tetrachloride.

The zirconium oxychloride solution formed on reacting zirconium tetrachloride with water is filtered to remove carried-over dust and silica formed by hydrolysis of silicon chlorides, then treated with hypochlorite to oxidize iron to the ferric state and scrubbed with methyl isobutyl ketone to extract ferric chloride. The iron-free stream is treated with ammonium thiocyanate and aqueous ammonia and introduced into the solvent extraction plant, where the hafnium, molybdenum and some uranium and titanium are extracted into methyl isobutyl ketone. The aqueous stream containing the zirconium is treated with ammonium sulfate and sulfuric acid to precipitate zirconium as a sulfate and to adjust the acidity, then filtered. Aluminum, uranium and titanium remain with the solution in this step. Precipitated zirconium sulfate is repulped with ammonia to convert the sulfate to hydrated zirconium oxide, then calcined to produce anhydrous zirconium oxide. Impurities removed in these steps are listed on Sheet 4.

The zirconium oxide is mixed with petroleum coke and chlorinated to zirconium tetrachloride. Zirconium is separated from the last traces of silicon and from some phosphorus in this step, but removal of iron (mostly from contamination from the equipment) and of the remaining phosphorus is effected by subliming the zirconium tetrachloride in the presence of hydrogen. Sheet 5 summarizes these facts, and leads to the next steps.

Most of the resulting magnesium chloride and excess magnesium are separated mechanically and the remainder removed by vacuum distillation. In this step, and the subsequent ones of consolidation by arc melting, then of fabrication, there is effectively no further opportunity for impurity removal. Rather, these steps are carried out so as to minimize pick-up of undesirable impurities, particularly oxygen and nitrogen, but also many other potentially contaminating materials too numerous to list.

ANALYSIS

Throughout the zirconium extraction process, analyses are conducted to verify that impurities of concern have been successfully rejected. Further analyses are performed on the metal product after consolidation and during and after fabrication. Table 4 lists the methods used for zirconium analysis, and Tables 5 through 8 give the elements (or element) for which each method is used, as well as the low reporting limit for each element and the precision of the determination at the reporting limit. All of the methods are capable of detecting the elements for which they are used to levels lower than the reporting limit; some have been refined so that impurities can be confidently measured in the range of parts per billion.

ACKNOWLEDGEMENTS

Figures 1a, 1b, 3a, 3b, 4 and 5 are taken from "Oxidation of Zirconium & its Alloys", B. Cox, in Advances in Corrosion Technology, Vol. 5, M. G. Fontana and R. W. Staehle, Eds., Plenum Press, New York, 1970.

Figures 2a and 2b are taken from "The Development of Zirconium Alloys", S. Kass, in Corrosion of Zirconium Alloys, ASTM Special Publication No. 368, American Society for Testing and Materials, 1916 Race St., Philadelphia, PA, 1964. Republished by University Microfilms, Ann Arbor, MI, 1979.

TABLE 1

ZIRCONIUM INGOT SPECIFICATIONS
MAXIMUM IMPURITIES, PPM

IMPURITY	ASTM B350 R60901	CANADIAN Zr-2.5Nb	OTHERS
Al	75	75	
B	0.5	0.5	
C	270	500	
Cd	0.5	0.5	
Cl	---	20	
Co	20	20	
Cr	200	200	
Cu	50	50	
Fe	1500	1200	
Gd	---	---	5
H	25	25	
Hf	100	200	50
Mg	20	20	
Mn	50	50	
Mo	50	50	
N	65	80	
Ni	70	70	
P	---	---	50,30
Pb	---	130	50
Si	120	120	
Sm	---	---	10
Sn	50	200	
Ta	---	---	200,100
Th	---	---	7
Ti	50	50	
U	3.5	3.5	
V	50	50	
W	100	100	

EFFECTS OF IMPURITIES

ON

* NUCLEAR PROPERTIES

B, Cd, Gd, Hf, Sm, U

* MECHANICAL PROPERTIES

Sn, Nb, Al, O, N, C, Si, P, H

* CORROSION PROPERTIES

N, C, Al, Ag, Co, Cr, Cu, Fe, Ge, Mn,
Nb, Ni, O, P, Pb, Pd, Sb, Sn, Ti, V

TABLE 2

EFFECTS ON MECHANICAL PROPERTIES

CHANGE IN TENSILE PROPERTY IN LONGITUDINAL OR TRANSVERSE* DIRECTION, PER PPM OF EACH ATTRIBUTE, FOR NOTED CONCENTRATION-RANGE, FOR COLD ROLLED ZIRCALLOY-4 SHEET 3.2 mm THICK.

ATTRIBUTE	Sn	Fe+Cr	O*	C*	P*	Si*
RANGE	1.2-1.7%	2300-3600ppm	760-1950ppm	60-280ppm	7-22ppm	15-160ppm
ROOM TEMPERATURE						
Δ0.2% Y.S., $KPa \cdot ppm^{-1}$	3.3	-6.2	120	140	-680	-36
Δ U.T.S., $KPa \cdot ppm^{-1}$	-1.0	-4.8	120	130	-370	-57
Δ ELONGATION, $\% \cdot ppm^{-1}$	---	---	-0.007	---	-0.05	-0.006
316C						
Δ0.2% Y.S., $KPa \cdot ppm^{-1}$	2.9	---	30	-43	-690	120
Δ U.T.S., $KPa \cdot ppm^{-1}$	1.2	3.4	40	---	-320	-31
Δ ELONGATION, $\% \cdot ppm^{-1}$	-0.0005	-0.002	(-0.002)	-0.007	+0.1	-0.01

CORROSION EFFECTS OF IMPURITIES

* IMPURITIES WITH A MAJOR DELETERIOUS EFFECT

  N, C

* IMPURITIES WITH A MAJOR BENEFICIAL EFFECT

  Sn, Fe, Cr, Ni

* IMPURITIES WITH A MINOR OR UNCERTAIN EFFECT

  Al, Ag, Co, Cu, Ge, Mn, Nb, O, P, Pb, Pd, Sb, Ti, V

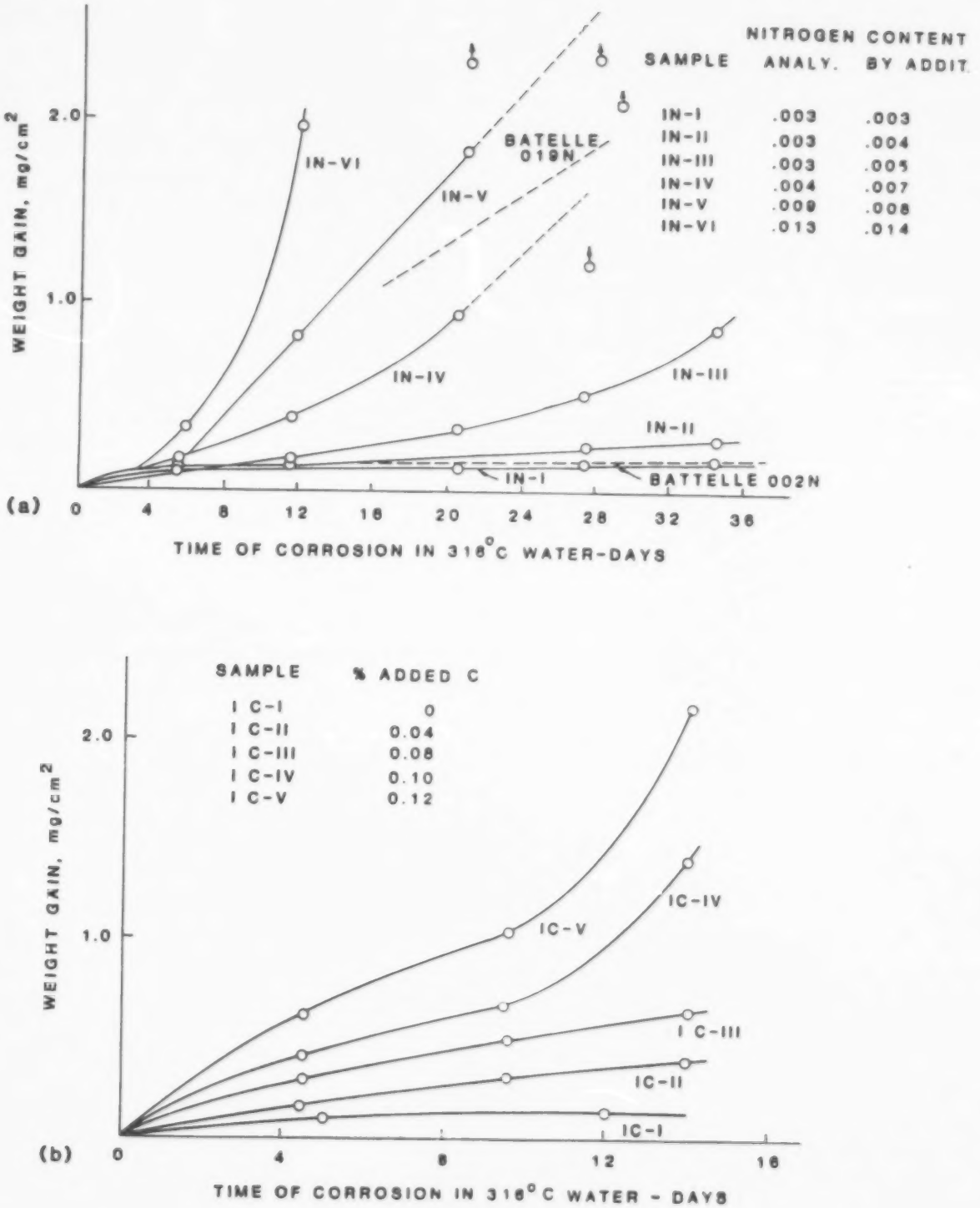


FIG. 1 EFFECT OF (a) NITROGEN AND (b) CARBON ON THE CORROSION RESISTANCE OF ZIRCONIUM IN 316° C WATER.

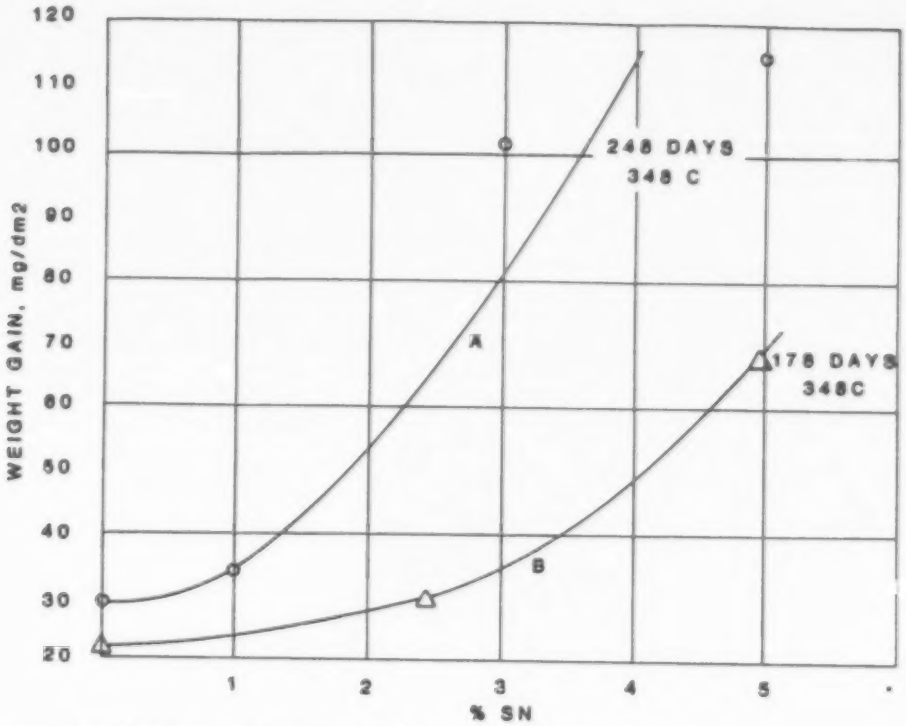


FIG. 2a EFFECT OF TIN CONTENT UPON CORROSION RESISTANCE OF CRYSTAL BAR ZIRCONIUM

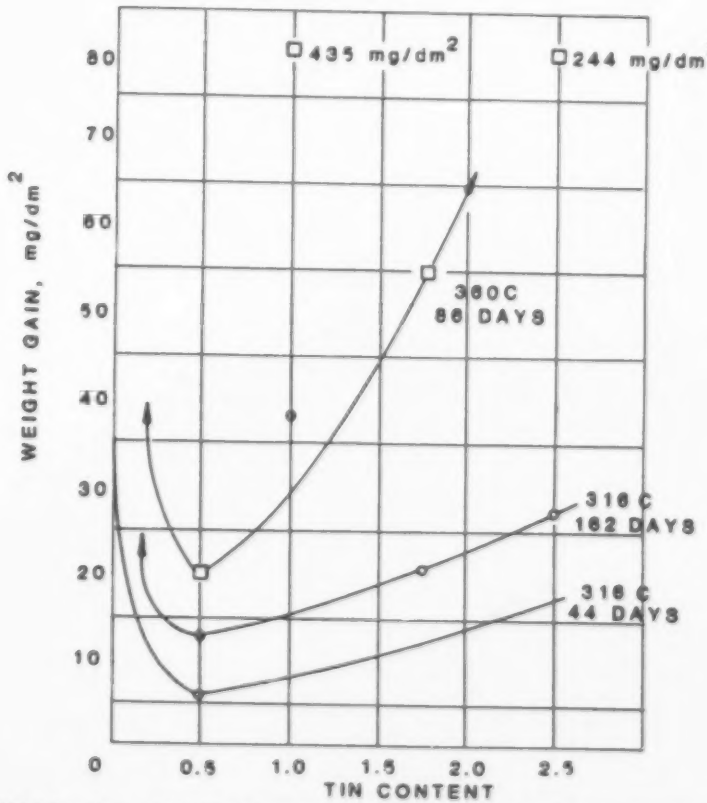


FIG. 2b EFFECT OF TIN CONTENT UPON CORROSION RESISTANCE OF OF SPONGE ZIRCONIUM CONTAINING 60 ppmN.

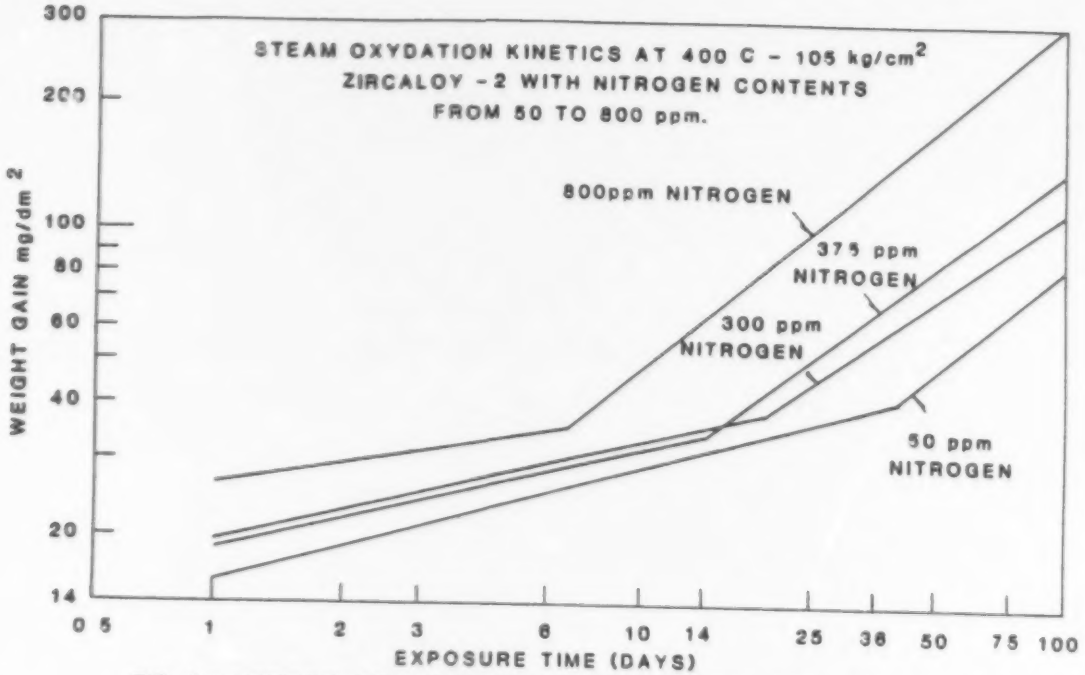


FIG. 3a EFFECT OF NITROGEN IMPURITY ON THE OXIDATION OF ZIRCALOY-2 IN 400C STEAM.

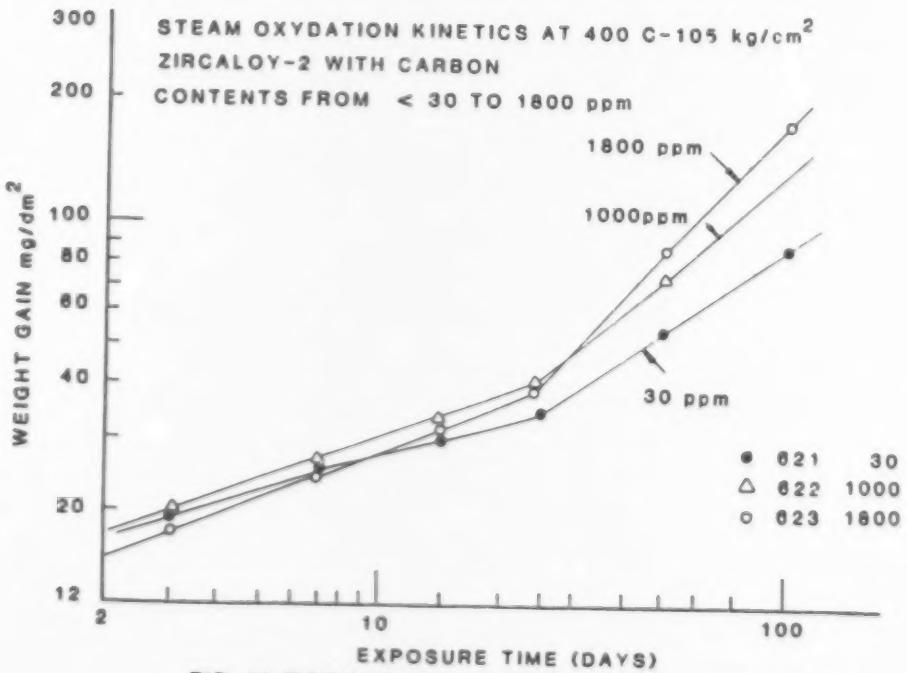


FIG. 3b EFFECT OF CARBON IMPURITY ON THE OXIDATION OF ZIRCALOY-2 IN 400C STEAM.

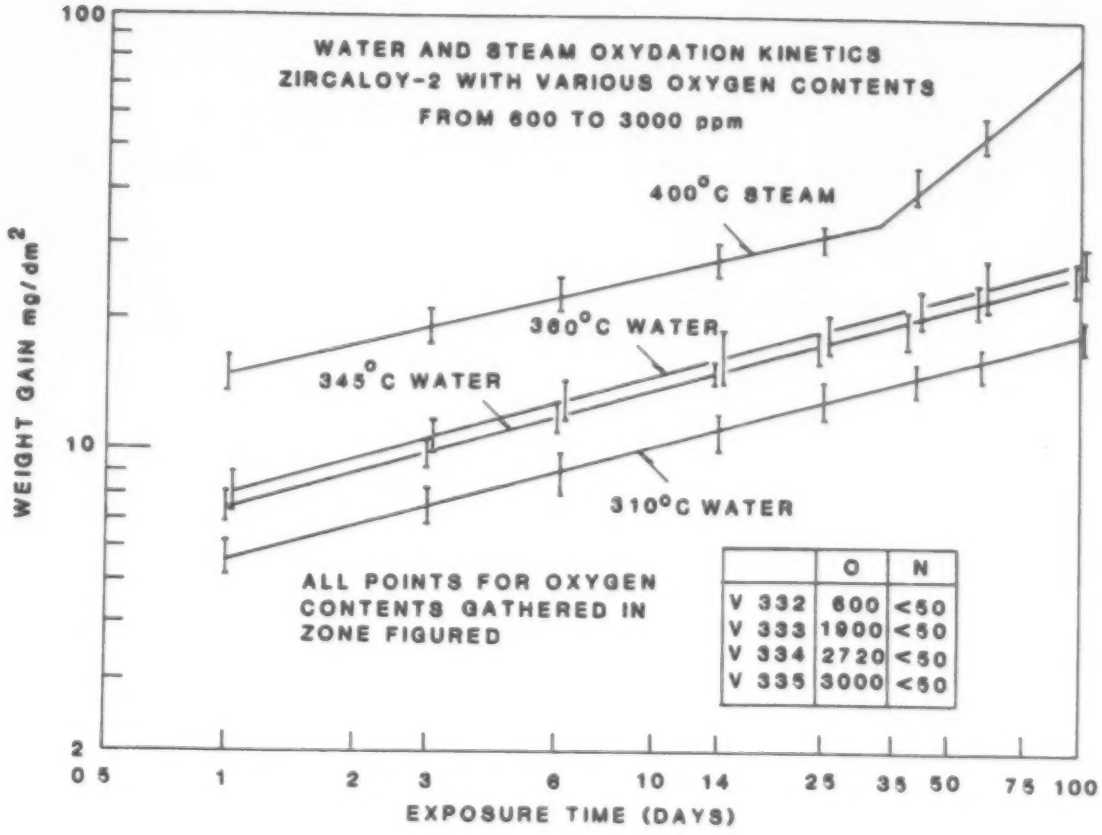


FIG. 4 EFFECT OF OXYGEN IMPURITY ON THE OXIDATION OF ZIRCALOY-2 IN 400° C STEAM

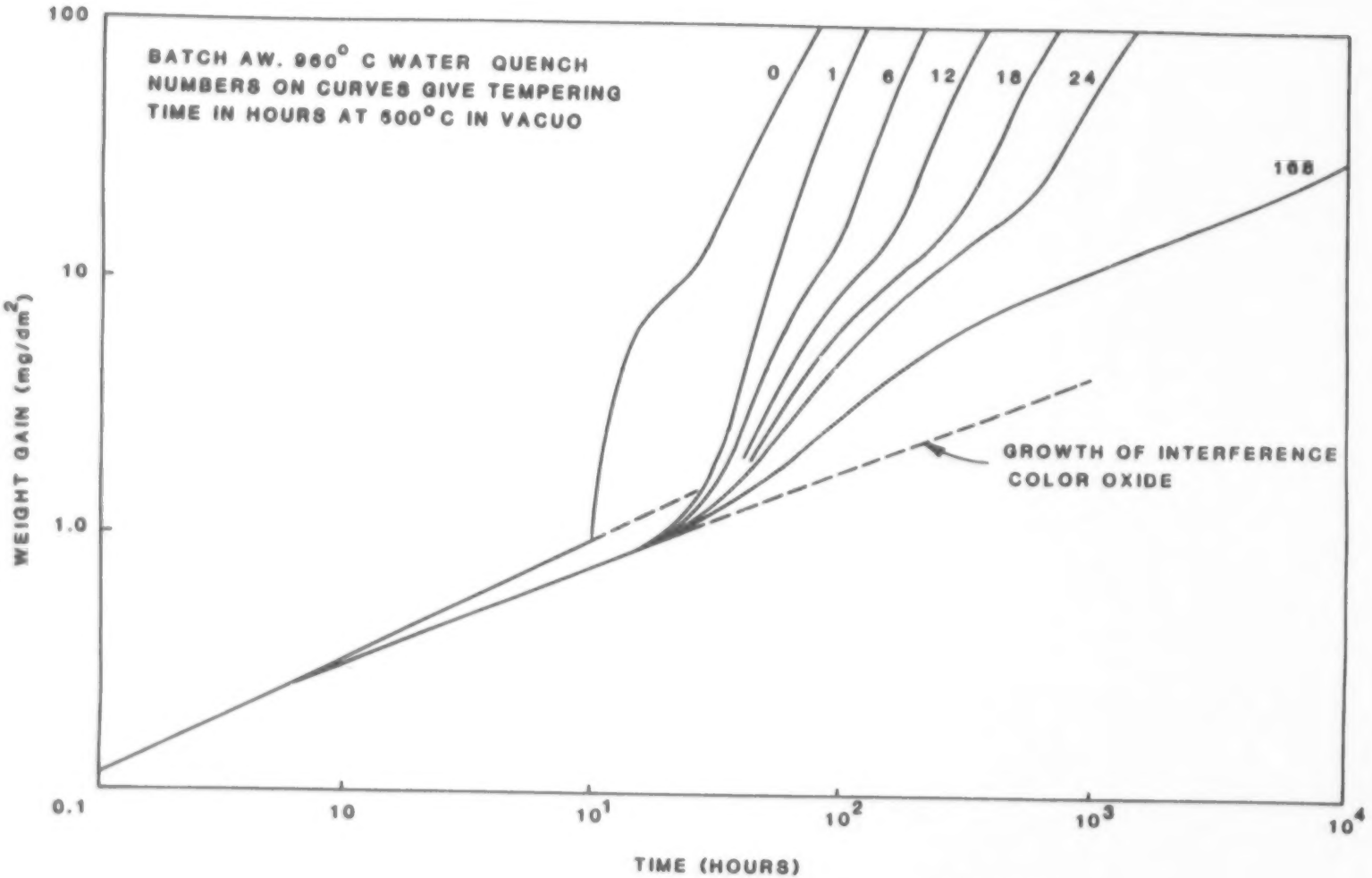


FIG. 5 EFFECT OF TEMPERING TIME ON THE OXIDATION OF Zr-2.5% Nb ALLOY SPECIMENS IN MOIST AIR AT 300°C.

TABLE 3

SPECIFICATION FOR ZIRCON

$ZrSiO_4$

ZrO_2+HfO_2	$\geq$ 66%
Al_2O_3	$\leq$ 0.35%
Fe_2O_3	$\leq$ 0.2%
P_2O_5	$\leq$ 0.08%
SiO_2 (uncombined)	$\leq$ 0.5%
TiO_2	$\leq$ 0.25%
U + Th	< 0.05%

MINOR IMPURITIES IN ZIRCON

ZIRCON USUALLY CONTAINS THE FOLLOWING IMPURITIES IN THE RANGE OF 10-250 ppm:

Ca, Cr, Co, Cu, Mg, Mn, Mo, Nb, Ni, Pb, Sr, Ta, W, Zn, Rare Earths

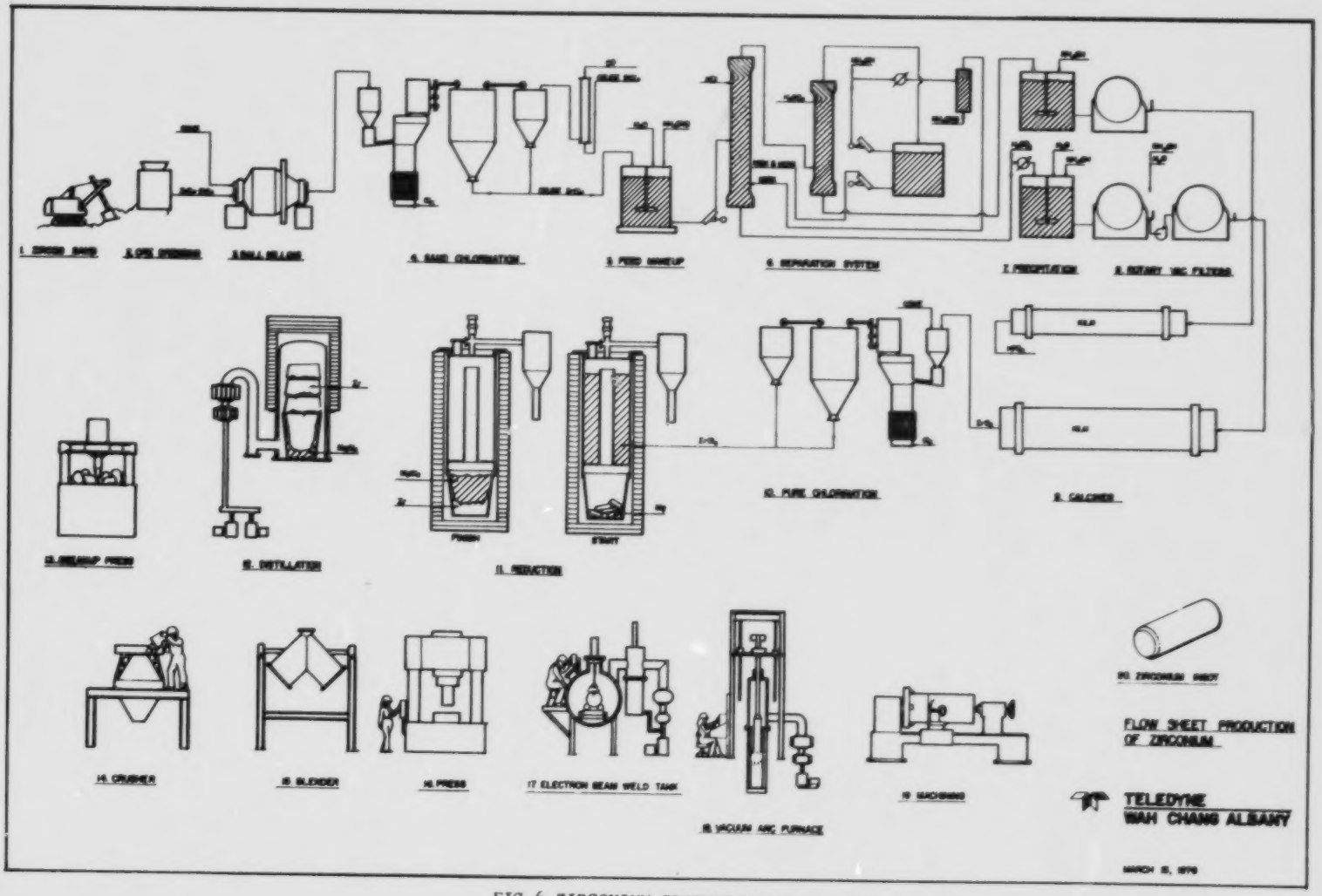


FIG.6 ZIRCONIUM PRODUCTION FLOW SHEET

Zirconium Production

Manufacturing Sequence

1. Zircon Sand ($ZrSiO_4$)
Zirconium is fairly common in the earth's crust, being more plentiful than some of the more familiar metals such as nickel and copper. Zircon (zirconium orthosilicate), the principal and most abundant zirconium-bearing mineral, is widely distributed throughout the world. Australia is currently the major supplier of this important mineral.

2. Ore Dressing
Zircon is recovered as a coproduct with rutile and ilmenite. Flotation, electrostatic, and magnetic processes are employed to separate these minerals.

3 Ball Milling
Zircon sand and stoichiometric quantities of carbon in the form of coke are mixed and ground together in a ball mill to provide an intimate mixture within a specified particle size range.

4. Sand Chlorination
The zircon sand/coke mixture is reacted with chlorine (Cl_2) at about 1200° C to produce zirconium tetrachloride ($ZrCl_4$) and silicon tetrachloride ($SiCl_4$) according to the following chemical reaction:

$$ZrSiO_4 + 4C + 4Cl_2 \longrightarrow ZrCl_4 + SiCl_4 + 4CO$$

Zirconium tetrachloride and silicon tetrachloride are subsequently separated by partial condensation of the chlorinator off-gas. Silicon tetrachloride is treated as a byproduct of the process.

5. Feed Makeup
Zirconium tetrachloride containing approximately two percent hafnium tetrachloride, a major impurity and a sister element of zirconium, is dissolved in water. The feed solution is adjusted to a specific concentration and filtered to remove suspended solids (fine sand and carbon). This solution is then transferred to the separation system.

6. Separation System
The separation system is composed of a series of extraction, stripping, and scrubbing columns which separate, via liquid-liquid extraction, the elements zirconium and hafnium. Although these sister elements are very similar chemically, they differ markedly in their nuclear properties. Zirconium acts like a window to thermal neutrons while hafnium absorbs large quantities of neutrons. Consequently, there is a need for their separation.

7. & 8. Precipitation and Rotary Vacuum Filters
Solutions containing hafnium and zirconium are collected in their own storage tanks and handled separately. The aqueous zirconium solution is precipitated with sulfuric acid to form a hydrous zirconium sulfate. This slurry is filtered on a rotary filter; the filter cake is repulped with aqua ammonia to form hydrous zirconia and is filtered again to remove sulfate ions.

Hafnium precipitation is effected by the addition of ammonia to an aqueous solution of hafnium sulfate.

9. Calciner
Hydrous zirconia from the last wash filter is pumped to a gas-fired rotary kiln which operates at a temperature of approximately 1000°C (1832°F) The calcined product, zirconium oxide (ZrO_2), is collected in containers at the discharge end of the calciner.

Hafnium is also processed through a calciner to obtain hafnium oxide (HfO_2).

10. Pure Chlorination
Zirconium oxide and stoichiometric quantities of carbon (coke) are intimately blended and reacted with chlorine according to the following chemical reaction:

$$ZrO_2 + 2C + 2Cl_2 \longrightarrow ZrCl_4 + 2CO$$

Several impurities including aluminum, iron and titanium are reduced during this chlorination operation.

11. Reduction
Zirconium tetrachloride is reacted with metallic magnesium in a classic Kroll reduction according to the following chemical reaction:

$$ZrCl_4 + 2Mg \longrightarrow Zr + 2MgCl_2$$

Magnesium chloride ($MgCl_2$) is formed as a byproduct.

12. Distillation
The magnesium chloride byproduct is physically removed from the Kroll reduction reaction products. The remaining zirconium regulus is loaded into a distillation furnace. Here the surplus magnesium is distilled from the zirconium metal, leaving a porous sponge-like material.

13. Breakup Press
The zirconium sponge regulus is broken into smaller pieces which are suitable as feed to the crushing operation. Hand grading of sponge product is performed during this operation to upgrade quality.

14. Crusher
Sponge is crushed from approximately four inch material down to minus three-quarter inch. Fines are rejected at this point.

15. Blender
Individual runs of zirconium sponge are blended together to meet production specification requirements.

16. Press
Zirconium sponge and alloying elements are mixed together and pressed into a 14" diameter × 5" thick compact.

17. Electron Beam Weld Tank
Sponge compacts and scrap billets are electron beam welded to form arc melt electrodes.

18. Vacuum Arc Furnace
Welded electrodes are melted into ingots (23" dia. × 13,000#) by the consumable arc melting process. Doubling melting ensures homogeneity.

19. Machining
Cast ingots are machined to remove surface porosity and melting anomalies.

20. Zirconium Ingot
Final machined ingots are then fabricated into wrought product by forging, hot rolling, cold rolling or extrusion.

REMOVAL OF IMPURITIES IN PROCESSING

CHLORINATION/$ZrCl_4$ CONDENSATION

* ELEMENTS WITH CHLORIDES LESS VOLATILE THAN $ZrCl_4$

  e.g. Mg, Ca, Mn, Co, Ni, Sr, Ra, Th, Cr, Pb, Y, Rare Earths

* ELEMENTS WITH CHLORIDES MORE VOLATILE THAN $ZrCl_4$

  e.g. Si, S, B

* ELEMENTS WITH CHLORIDES COMPARABLY VOLATILE TO $ZrCl_4$, OR WITH CHLORIDES THAT COMBINE WITH $ZrCl_4$, TEND TO REPORT WITH $ZrCl_4$

  e.g. Fe, U, Some Al & Ti, a Little Si, and P

REMOVAL OF IMPURITIES IN PROCESSING

Zr/Hf SEPARATION

* FEED MAKE-UP/FILTRATION:

  Si, CARRIED-OVER DUSTS, & IN A SEPARATE STEP, Fe.

* Zr/Hf SEPARATION COLUMNS:

  Mo, Ti, Some U (WITH Hf)

* ZrO_2 PRECIPITATION/RECOVERY:

  Al, Ti, U, Pb, Cu, &c.

REMOVAL OF IMPURITIES IN PROCESSING

* ZrO_2 CHLORINATION/$ZrCl_4$ SUBLIMATION

  Fe, P

NO IMPURITY REMOVAL IN

* REDUCTION

* ARC-MELTING

* FABRICATION

PRECAUTIONS MUST BE TAKEN TO AVOID CONTAMINATION IN THESE STEPS.

TABLE 4

ANALYSIS OF ZIRCONIUM

METHODS

* ARC-SOURCE OPTICAL EMISSION SPECTROSCOPY: OES

* DC PLASMA-SOURCE EMISSION SPECTROSCOPY: DCP

* INDUCTION-COUPLED PLASMA-SOURCE MASS SPECTROSCOPY: ICP-MS

* COMBUSTION IN OXYGEN, CO_2 BY I.R. ABSORBTION: C-IR

* FUSION WITH Pt IN INERT GAS, CHROMATOGRAPHY, CO_2 BY I.R. ABSORBTION, H_2 & N_2 BY THERMAL CONDUCTIVITY: F-GC

* KJELDAHL DISTILLATION, N AS NH_3 BY TITRATION: K

* ATOMIC ABSORBTION SPECTROSCOPY: AA

* X-RAY FLUORESCENCE DETERMINATION OF PRECIPITATED AgCl: X-Ag

TABLE 5

ELEMENTS BY METHOD

ARC SOURCE OPTICAL EMISSION SPECTROSCOPY

OES

ELEMENT	LOW REPORTING LIMIT, PPM	PRECISION, %
B	0.25	8
Cd	0.25	10
Co	7	10
Cr (LOW LEVEL)	50	7
Mn	25	10
Mo	10	10
Ni (LOW LEVEL)	35	5
Pb	25	10
Sn (LOW LEVEL)	10	10
V	25	10
W	25	10
Zn	50	10

TABLE 6

ELEMENTS BY METHOD

DC PLASMA SOURCE EMISSION SPECTROSCOPY

DCP

ELEMENT	LOW REPORTING LIMIT, PPM	PRECISION, %
Al	35	5
Cr (ALLOY ADDN.)	--	5
Cu	10	7
Fe	50	5
Hf	25	5
Nb	50	5
Ni (ALLOY ADDN.)	--	5
Si	10	5
Sn (ALLOY ADDN.)	--	4
Ta	50	5
Ti	25	5

TABLE 7

ELEMENTS BY METHOD

INDUCTION-COUPLED PLASMA-SOURCE MASS SPECTROSCOPY

ELEMENT	REPORTING LIMIT, PPM	PRECISION, %
Gd	2.5	10
Sm	5	5
Th	3.5	5
U (TOTAL)	1	5
U^{235}	0.01	5

TABLE 8

ELEMENTS BY METHOD

COMBUSTION (C-IR), FUSION (F-GC), KJELDAHL (K), ATOMIC ABSORBTION (AA), FLAME IONIZATION (FID), X-RAY FLUORESCENCE (x-Ag)

ELEMENT	METHOD	LOW REPORTING LIMIT, PPM	PRECISION, %
C	C-IR	30	5
H	F-GC	5	5
N	F-GC	5	10
O	F-GC	50	5
N	K	5	10
Na	AA	10	5
P	FID	3	10
Cl	x-Ag	5	20

ZIRCONIUM ISOTOPE SEPARATION
PANEL DISCUSSION

The problems involved in isotope enrichment of zirconium and the potential applications of isotopically enriched zirconium were discussed by a panel involving Ed Price (Candu Ops), George Field (COG), John Haygarth (Director of Research, Wah Chang), Craig Simpson and Ken Woodall (both of Ontario Hydro Research Division.) Several of the conference attendees also contributed to the discussion.

Ken Woodall discussed the value of zirconium-91 depleted zirconium in Candu reactor parts and Ed Price discussed where this zirconium could best be used first in a Candu reactor. John Haygarth discussed the production and purification of zirconium. (His overheads appear elsewhere in this document.)

During the course of informal discussions Ed Price suggested a way to overcome the problems of containing high temperature liquid zirconium in a plasma centrifuge. (Both he and John Haygarth pointed out that in the zirconium processing industry liquid zirconium is often suspended magnetically. This will overcome the problem of how to contain a zirconium plasma at 3000 C without contamination. Professor Jay Hirschfield (of the Hebrew University of Jerusalem who leads a group that is developing the plasma centrifuge to separate zirconium isotopes and other heavy metal isotopes) indicated that he would attempt to construct a zirconium metal feed ion source based on magnetic levitation of zirconium. He indicated that this was the main problem remaining in the adaptation of plasma centrifuge technology to zirconium isotope separation.

Another suggestion (from Ed Price and George Field) is that the long term goal of this project should not initially be to prepare and test zirconium-91 depleted pressure tubes. Instead we should modify that goal to aim at the calandria tubes. Thicker calandria tubes would greatly reduce pressure tube sag and increase the safety margins in Candu reactors when pressure tubes crack. They suggested that it would be much easier to qualify a calandria tube than a pressure tube for in-reactor use. It would also take much less isotopically processed zirconium to make a calandria tube than to make a pressure tube, not only because calandria tubes use less metal than pressure tubes, but also because calandria tubes are made of welded sheet zirconium rather than being extruded as a tube.

In addition to the plasma centrifuge, two other methods of making zirconium-91 depleted zirconium, were discussed briefly. The most elegant method, atomic vapour laser isotope separation, has been demonstrated for zirconium isotope separation by Peter Hackett's group at the National Research Council in Ottawa. This method could also make use of the magnetic levitation technology discussed above to produce contamination-free zirconium beams. Another method is solvent extraction. (This is the process used to remove hafnium from zirconium at Teledyne Wah Chang and Western Zirconium.) Preliminary research at Westinghouse has indicated that this type of process could be used to separate zirconium isotopes as well. Some work is planned in this area at Teledyne Wah Chang and at Ontario Hydro Research Division.

HEAVY WATER PRODUCTION BY THE CIRCE PROCESS

Alistair Miller
AECL
Chalk River Nuclear Laboratories
Chalk River, Ontario, K0J 1J0

The Heavy Water Grail

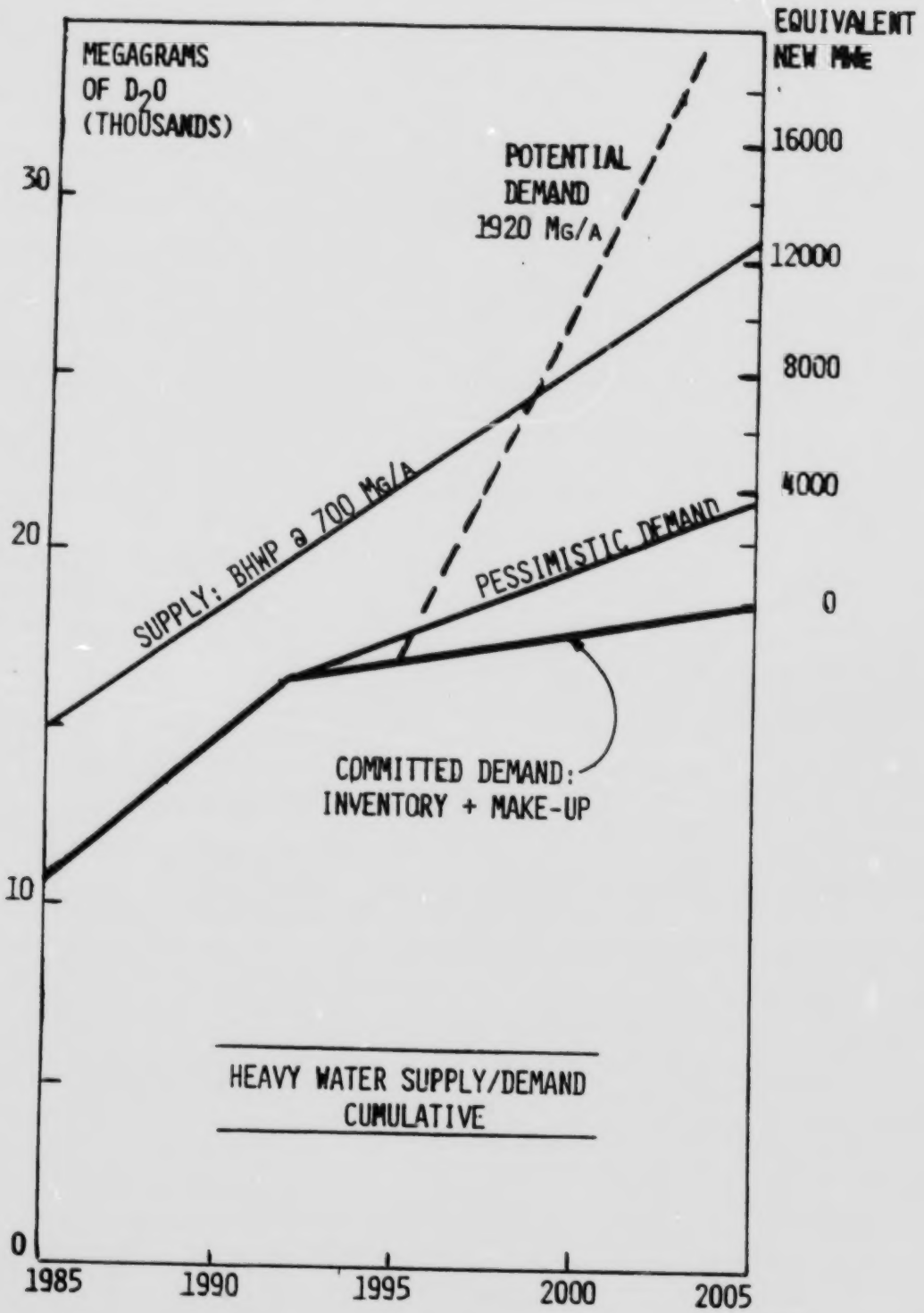
$200/kg or less.

FOUND*

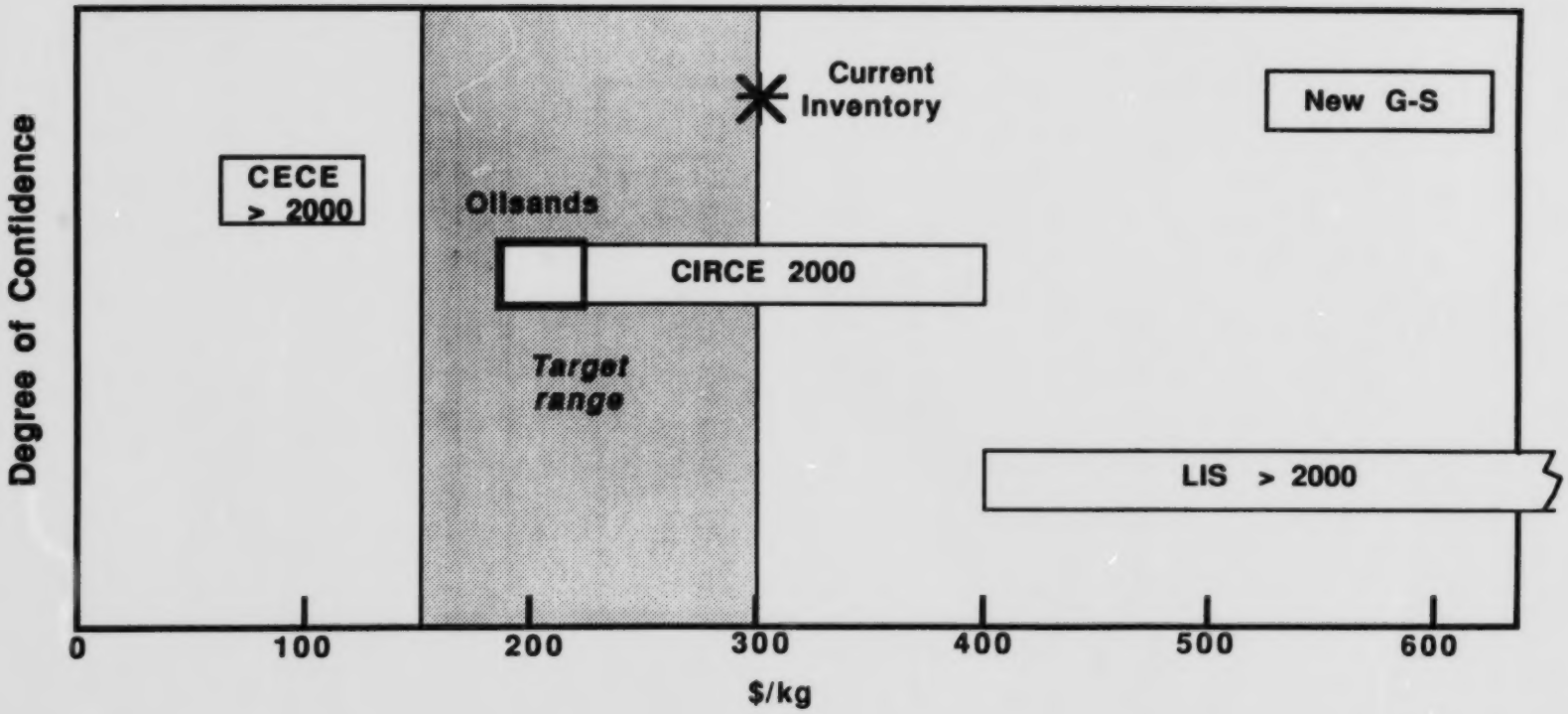
FOUND
FOUND
FOUND
FOUND
FOUND
FOUND
FOUND

What should we do with it?

*** Subject to industrial authentication**


MEGAGRAMS
OF D_2O
(THOUSANDS)
EQUIVALENT
NEW MWe
30
20
10
0
16000
12000
8000
4000
0
POTENTIAL
DEMAND
1920 MG/A
SUPPLY: BHWP @ 700 MG/A
PESSIMISTIC DEMAND
COMMITTED DEMAND:
INVENTORY + MAKE-UP
HEAVY WATER SUPPLY/DEMAND
CUMULATIVE
1985
1990
1995
2000
2005

HEAVY WATER COSTS



Natural Gas
STEAM REFORMER
CO SHIFT CONVERTER
CO_2 REMOVAL
METHANATOR
Oilsand
OILSANDS UPGRADER
Synthetic Crude
BOILER
Steam Water
HIGH PRESSURE HYDROGEN - WATER CATALYTIC EXCHANGE TOWER
Electrolysis
LOW PRESSURE HYDROGEN - WATER CATALYTIC EXCHANGE TOWER
Electrolysis
LOW PRESSURE HYDROGEN - WATER CATALYTIC EXCHANGE TOWER
D_2O
CIRCE - OILSANDS PLANT

How do Oilsands plants change D_2O prospects?

- Pure hydrogen = less catalyst
- Very big plants
- Many of them

} = significant amounts of D_2O

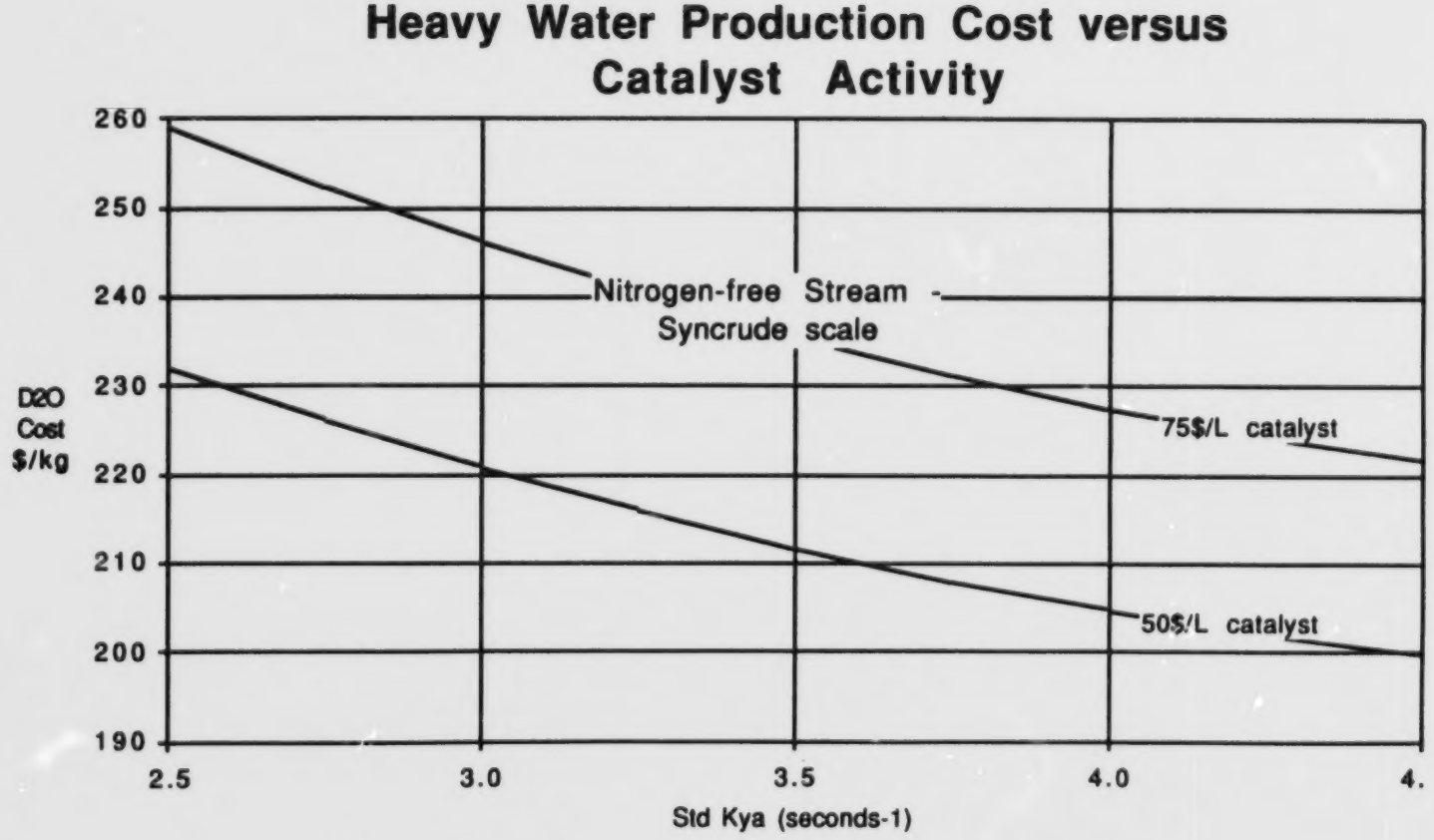
= Superior process economics

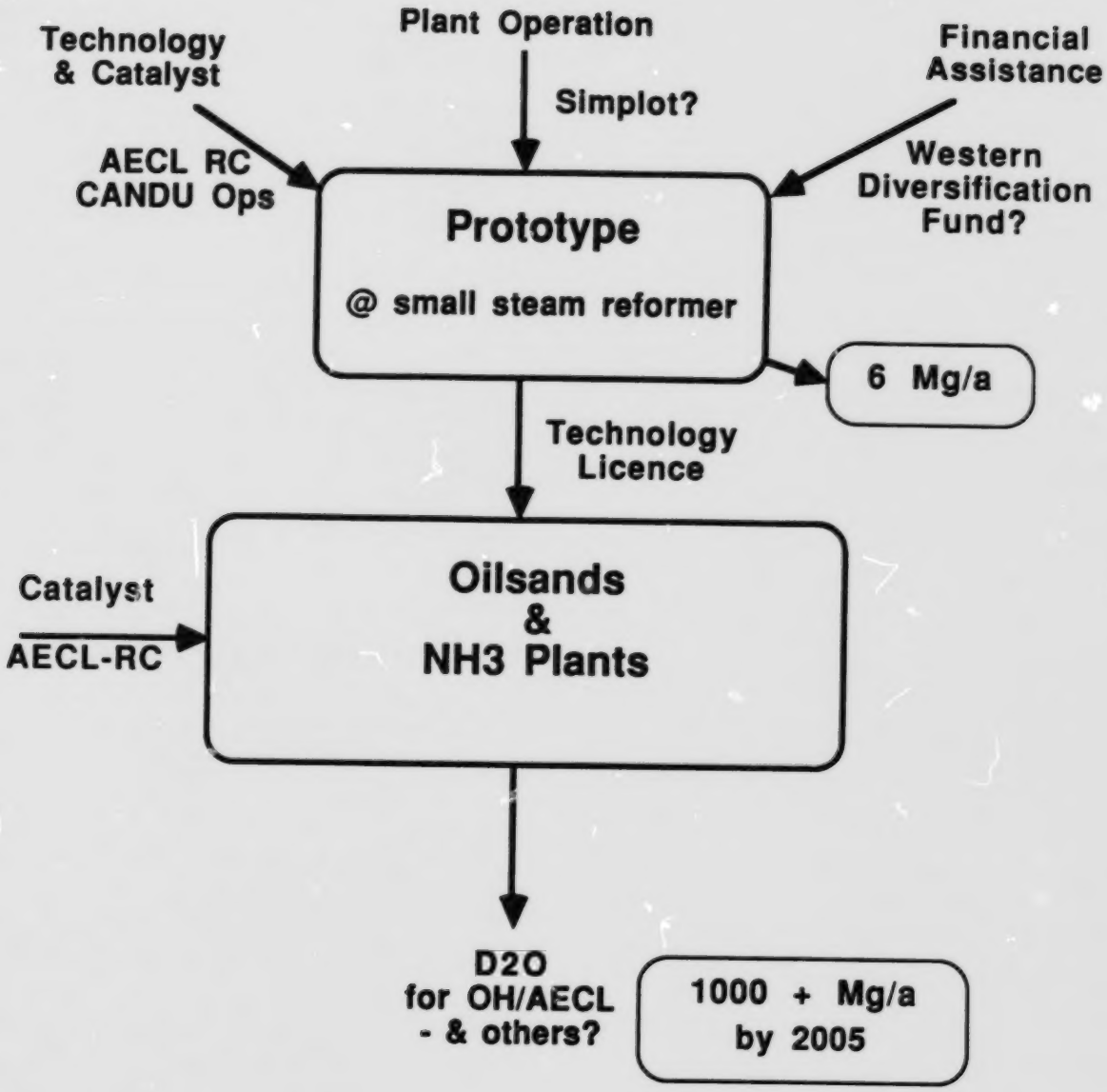
The Oilsands Resource

Improve H:C ratio

Syncrude: Equals 2.5 x 1500 Mg/d ammonia plant
Add two more by 1996 each equivalent to 1800 Mg/d NH3 plant
Oslo: Approved in principle - will use more hydrogen.
Lloydminster heavy oil: Proceeding
Other syncrude plants will follow.

1000 Mg Heavy Water/year


Heavy Water Production Cost versus
Catalyst Activity
260
250
240
230
220
210
200
190
D2O
Cost
$/kg
Nitrogen-free Stream -
Syncrude scale
75$/L catalyst
50$/L catalyst
2.5
3.0
3.5
4.0
4.
Std Kya (seconds-1)



Possible Anatomy of a CIRCE Heavy Water Industry

- Complete the Catalyst Development

- AECL-RC expects to complete in 1989/90
- Demonstration of ordered bed packing and of water distribution on larger scale

- Enrol the Oilsands Industry
  - Willingness to host
  - Allow for CIRCE at design phase
  - Confirmation of economics

Potential Benefits

- Diversified new source of low cost heavy water
- Nuclear industry for western Canada
- New product and revenue for hydrogen producers
- Exploit a new Canadian technology export potential

MOLECULAR LASER ISOTOPE SEPARATION AT RIKEN

Kazuo Takeuchi and Hideo Tashiro
Institute of Physical and Chemical Research
Bunri Kogaku
Wako, Saitama 351-01
Japan

Infrared multiphoton dissociation process of UF_6 was experimentally studied for the enrichment of uranium. Uranium hexafluoride gas was either contained in a static cell or recirculated in a loop connecting a supersonic expansion nozzle and a compressor. After the sample gas was irradiated with single- or multi-frequency laser beam the isotopic ratio of the residual gas was compared with that of the feed. The fractional conversion of the gas was measured simultaneously. It was found that the isotopic selectivity in dissociation (that corresponds to the enrichment in the product) was sufficiently high for one-stage enrichment.

MOLECULAR LASER ISOTOPE SEPARATION OF URANIUM AT RIKEN

PREPARATIVE STUDIES (1980-1984)

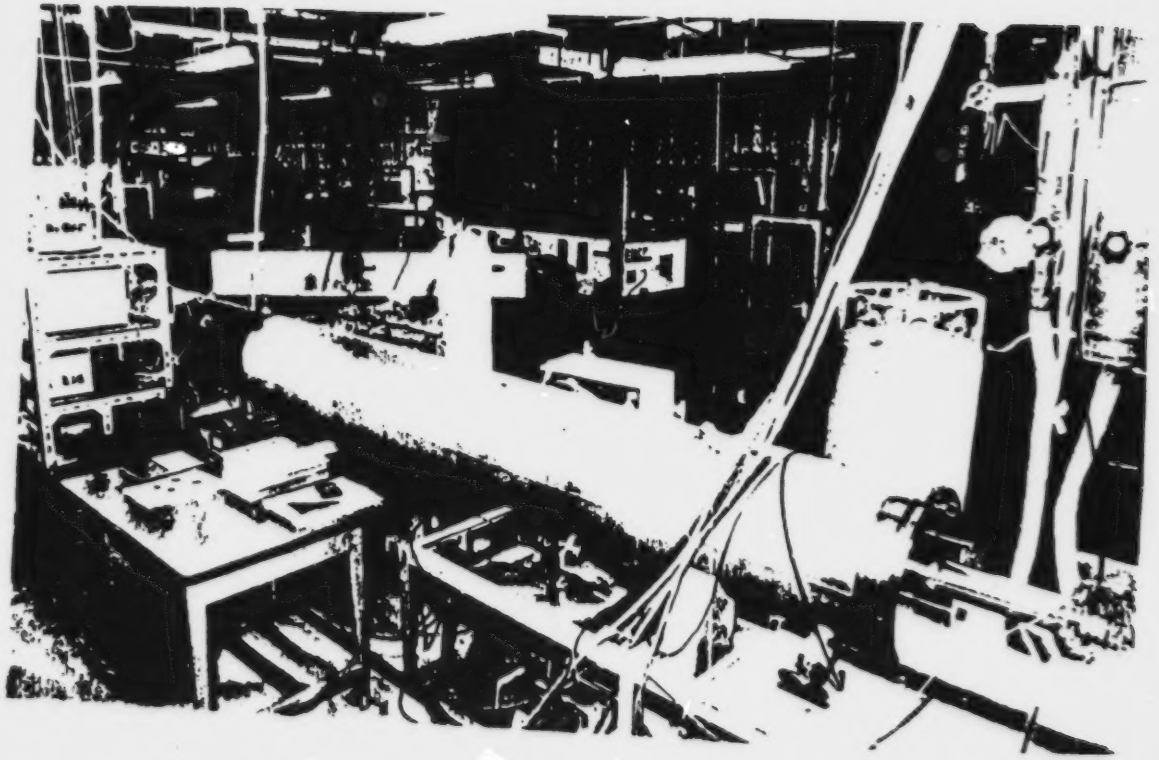
1) JET-COOLED SPECTRUM OF UF_6
2) DEVELOPMENT OF 16 μm LASER SYSTEM
3) ISOTOPE SEPARATION STUDY BY INFRARED MULTIPHOTON DISSOCIATION

SCIENTIFIC VERIFICATION (1985-1987)

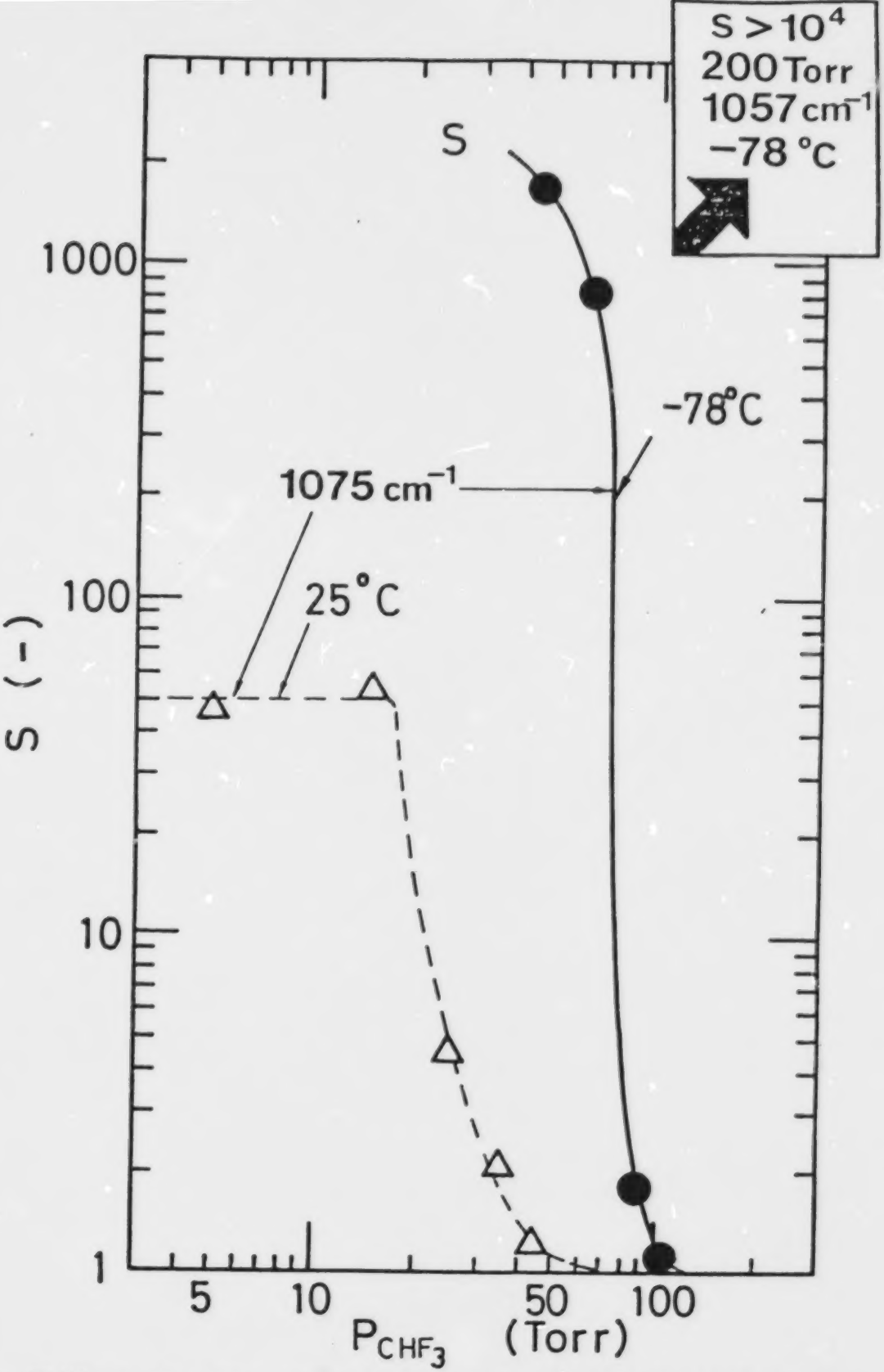
1) IMPROVEMENT OF LASER SYSTEM
2) MEASUREMENT OF SEPARATION FACTOR
3) STUDY OF RELATED CHEMICAL AND PHYSICAL PROCESSES

SCIENTIFIC DATA BASE (1988-1990)

1) DATA BASE FOR HIGHLY-EFFICIENT LASERS
2) DATA BASE FOR REACTION OPTIMIZATION
3) TECHNOLOGY TRANSFER TO PNC

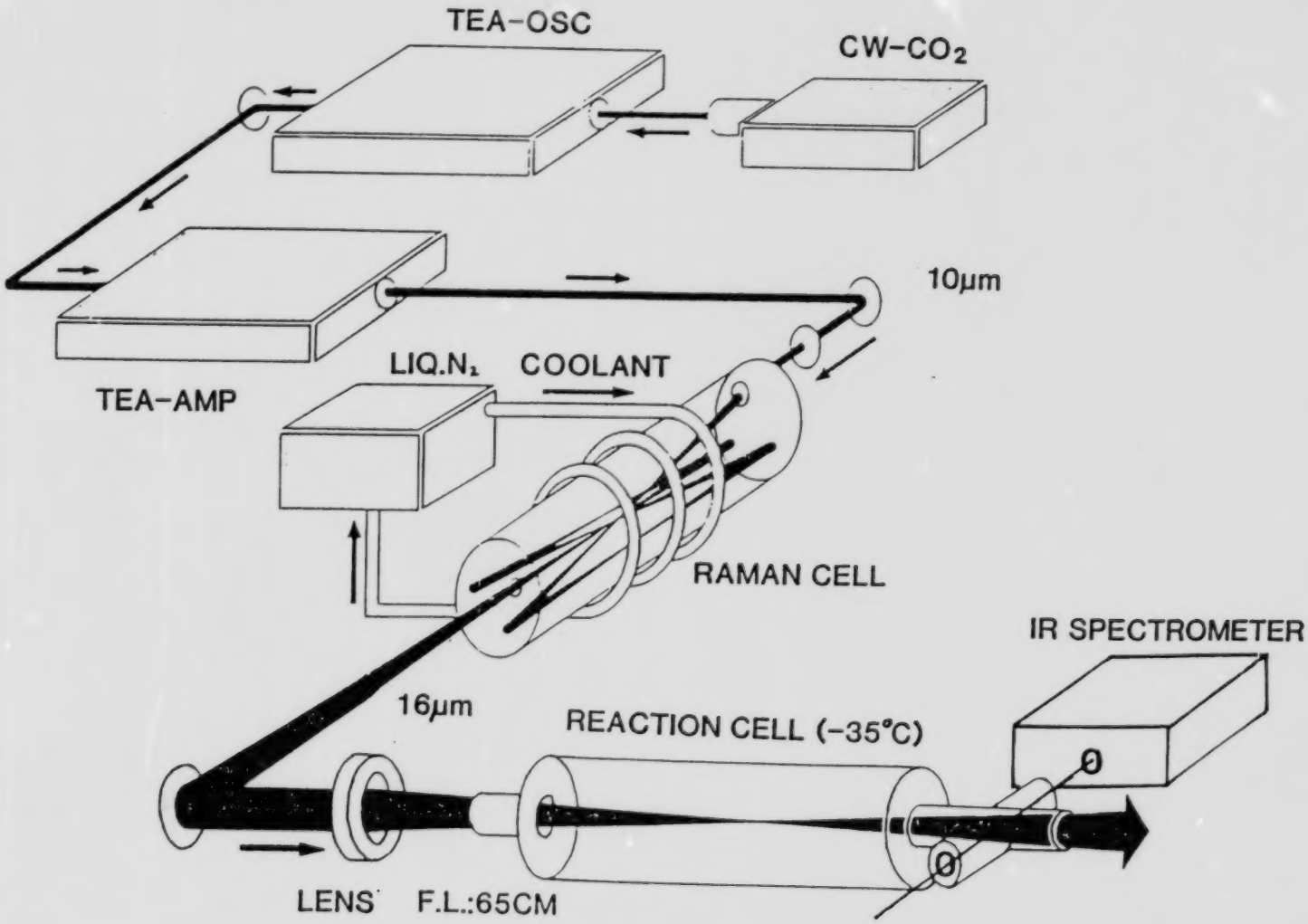


16μm Raman laser system at RIKEN (1984)



Tritium isotope separation by multiphoton dissociation of CTF_3 (1980)

Batch irradiation experiment



REACTION VOLUME PER PULSE :

$$V_i = \int_v q_i \, dV \quad (i = 5 \text{ or } 8) \qquad (1)$$

CONCENTRATIONS OF 235 AND 238 DECAY IN A WAY GIVEN BY

$$C_i = C_{i\,0} \exp(-V_i \, t / V_L) \qquad (2)$$

WHERE t IS THE NUMBER OF LASER PULSES AND V_L IS INVENTORY VOLUME.

$$b_i \equiv V_i / V_L \qquad (3)$$

REACTION SELECTIVITY S IS DEFINED BY

$$S = b_5 / b_8 = V_5 / V_8 \qquad (4)$$

S IS OBTAINED FROM

$$S = 1 - \ln \beta_{res} / \ln (1 - X_8) \qquad (5)$$

WHERE

$$\beta_{res} = \frac{(^{235}U / ^{238}U)\ \text{REACTANT BEFORE IRRAD.}}{(^{235}U / ^{238}U)\ \text{REACTANT AFTER IRRAD.}}$$

AND

X_8 = FRACTIONAL CONVERSION OF $^{238}UF_6$

WHEN $X_5,\ X_8 << 1$

$$S \cong \beta_{prod} \equiv \frac{(^{235}U / ^{238}U)\ \text{PRODUCT}}{(^{235}U / ^{238}U)\ \text{REACTANT BEFORE IRRAD.}}$$

Separation factor in IRMPD of UF_6

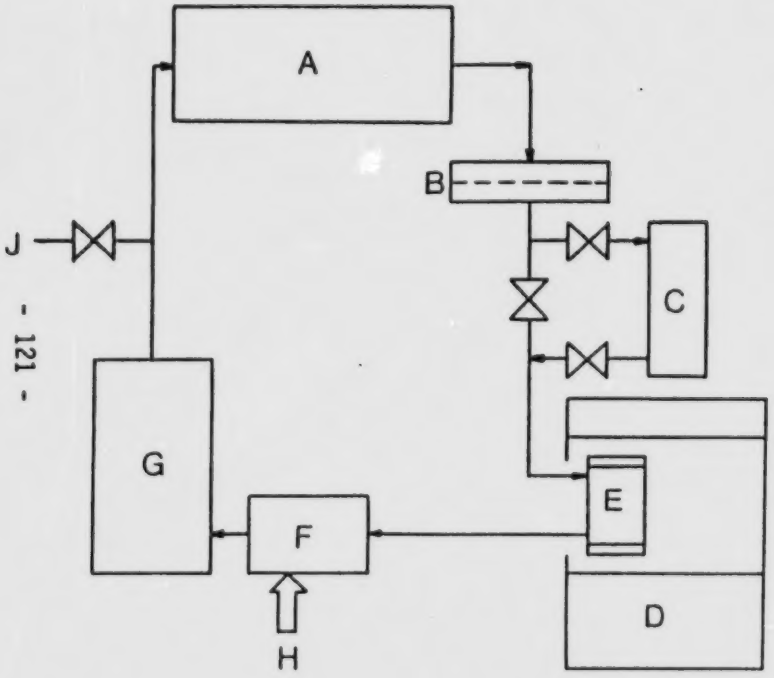
Experimental number	Laser wavenumber (cm^{-1})	UF_6 pressure (Torr)	H_2 pressure (Torr)	Fraction reacted	Separation factor (S)
1	627.8	0.2	0	0.09	1.043
2	627.8	0.2	1.0	0.59	1.025
3	627.8	0.38	1.0	0.43	1.014
4	626.6	0.38	1.0	0.44	1.011
5	629.0	0.38	1.0	0.24	1.014
6	975.9 (Breakdown)	90	239	0.37	1.000

$$^{235}UF_6 \xrightarrow{nh\nu} {}^{235}UF_5(s) + F \quad \cdots\cdots\cdots (1)$$

$$F + CH_4 \longrightarrow HF + CH_3 \cdots\cdots\cdots\cdots (7)$$

$$CH_3 + {}^{238}UF_6 \xrightarrow{\eta} CH_3F + {}^{238}UF_5(s) \quad \cdots\cdots (8)$$

$$CH_3 + CH_3 \xrightarrow{(1-\eta)} C_2H_6 \cdots\cdots\cdots\cdots\cdots (9)$$



Schematic diagram of experimental apparatus

A : compressors in series

B : filter

C : mass-flow meter

D : IR spectrophotometer

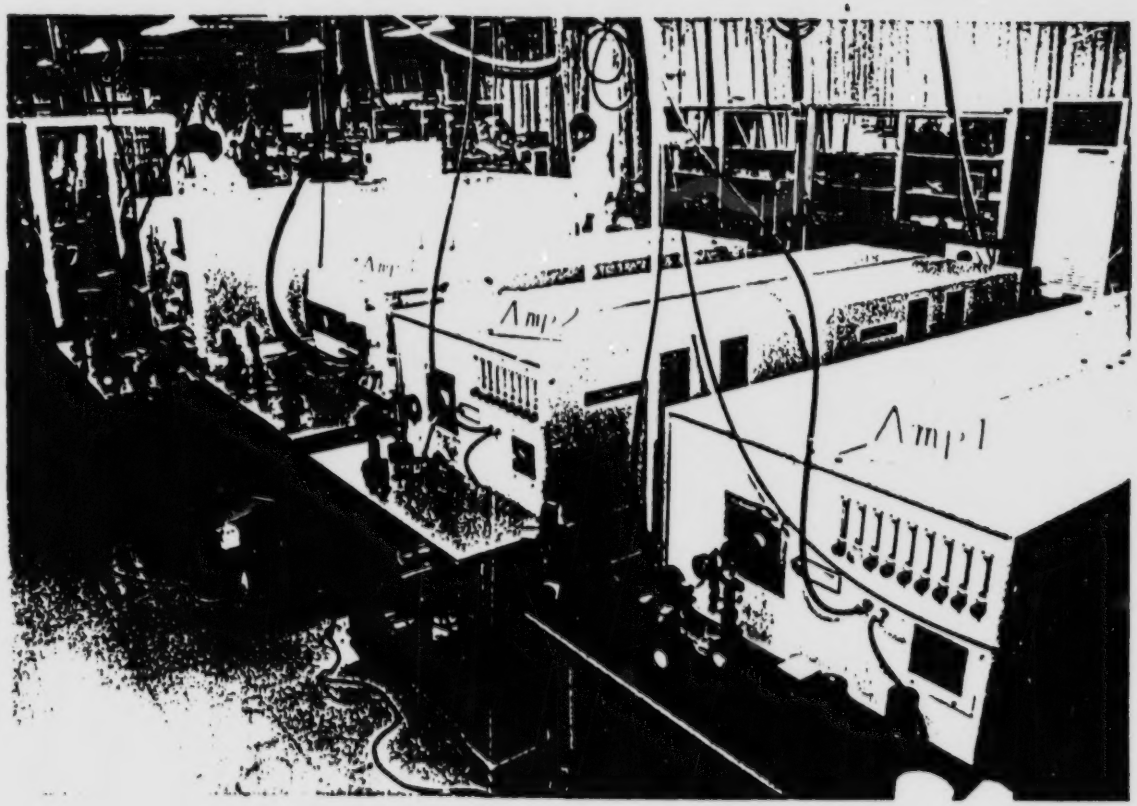
E : flow-cell with KCl windows

F : supersonic nozzle

G : low-pressure chamber

H : multi-frequency Raman laser beam

J : to vacuum line for UF6 supply and rcovery



実験に用いた１６ミクロンラマンレーザーシステム

16μm RAMAN LASER SYSTEM USED FOR ENRICHMET

Super-sonic nozzle reactor

89-49

The contrast ratio C_R can be defined by

$$C_R = \frac{(b_i) \text{ irradiation with both } \nu_1 \text{ and } \nu_2}{(b_i) \text{ irradiation with only } \nu_2}$$

Typical values of contrast ratio C_R in Riken's MLIS

UF_6 Temperature (K)	C_R
238	9.9
160	> 50

Typical values of separation factors

UF_6 temperature (K)	IR laser for excitation	IR laser for dissociation	separation factor S	
160	line-tunable	line-tunable	1.6	(1.7)
100	line-tunable	line-tunable	2.1	(2.3)
70	continuously tunable	line-tunable	4.2	(4.7)
			average	maximum

CONCLUDING REMARKS

1) IT WAS EXPERIMENTALLY DEMONSTRATED THAT INFRARED MULTIPHOTON DISSOCIATION OF UF_6 WAS ISOTOPICALLY SELECTIVE.

   SUFFICIENTLY HIGH SEPARATION FACTOR WAS OBSERVED FOR ONE-STAGE ENRICHMENT.

2) NO COLLECTION OF UF_5 PARTICLES WAS ATTEMPTED SO FAR.

3) STUDIES ON DATA BASE OF MLIS ARE NECESSARY.

LIS STUDIES AT CHALK RIVER NUCLEAR LABORATORIES

R.D. McAlpine
AECL
Chalk River Nuclear Laboratories
Chalk River, Ontario, K0J 1J0

PHYSICAL CHEMISTRY BRANCH

J.H. ROLSTON

LASER PHOTOCHEMISTRY SECTION

R.D. MCALPINE

IR MPD STUDIES	VISIBLE MP STUDIES
(D.K. EVANS)	L.W. GREEN
M.J. IVANCO	P.A. ROCHEFORT
G.A. MCRAE	M.H. SMYTH
B.A. YAMASHITA	F.C. MILLER
J.W. GOODALE	F.C. SOPCHYSHYN
P.E. LEE	

(E.B. SELKIRK)

(M.J. ST. AUBIN)

HEAVY WATER PRODUCTION USING LASERS

OBJECTIVES	(1) < $200 Kg
	(2) LARGE SCALE

ESTIMATED COST BREAKDOWNS

CAPITAL CHARGES (25%/a)	80%
LASER POWER	6%
LABOUR, WATER, STEAM, & MAINTENANCE	5%
WORKING MOLECULE MAKE-UP	5%
HELIUM MAKE-UP	2%
OTHER COSTS	2%
	100%

BREAKDOWN OF CAPITAL COSTS

CONTINGENCY, COMPLEXITY, DESIGN	33%
LASERS (@ $20 US/w)	28%
BUILDINGS, AND YARD,	12%
FRONT END	8%
ELECTRICAL SYSTEM	8%
LASER IRRADIATION	3%
COMPRESSORS	3%
OTHER COSTS	5%
	100%

IMPORTANT FACTORS IN ECONOMICS

1. HIGH OPTICAL SELECTIVITY
   - Loss of Photon
   - Loss of working molecules
   - Loss of selectivity
2. EXCHANGE CHEAP
3. MPD AT LOW FLUENCE
4. SEPARATION FACTORS HIGH
   - Loss of working molecules
5. CHEAP WORKING MOLECULES
6. LOW LASER CAPITAL COSTS
   < $20/w
7. MULTIPLE EQUIVALENT HYDROGEN ATOMS

CRITERIA

1. OPTICAL SELECTIVITY, $S(0) > 10^3$
2. RAPID CHEMICAL EXCHANGE WITH BULK SOURCE
3. EFFICIENT MPD AT LOW FLUENCE
4. STABLE PRODUCTS - NON EXCHANGE OF D
5. HEADS SEPARATION FACTORS > 10^4
6. POSITIVE NON-LINEAR OPTICAL PROPERTIES
7. WM CHEAP AND AVAILABLE @ $2/kg
8. WM RELATIVELY NON-TOXIC AND NON-EXPLOSIVE
9. DEUTERATED PRODUCTS EASILY SEPARATED
10. WM VOLATILE ENOUGH FOR GAS PHASE OPERATION AT OR NEAR ROOM TEMPERATURE
11. MONODEUTERATED BAND NEAR SPECIAL LINES FROM CO_2 OR OTHER LASER SOURCES (e.g., HX, NH_3, CH_4, RAMAN SHIFTED).
12. OTHER PROPERTIES MUST NOT PRECLUDE THE USE OF THE WORKING MOLECULE

INITIAL LIST (169)

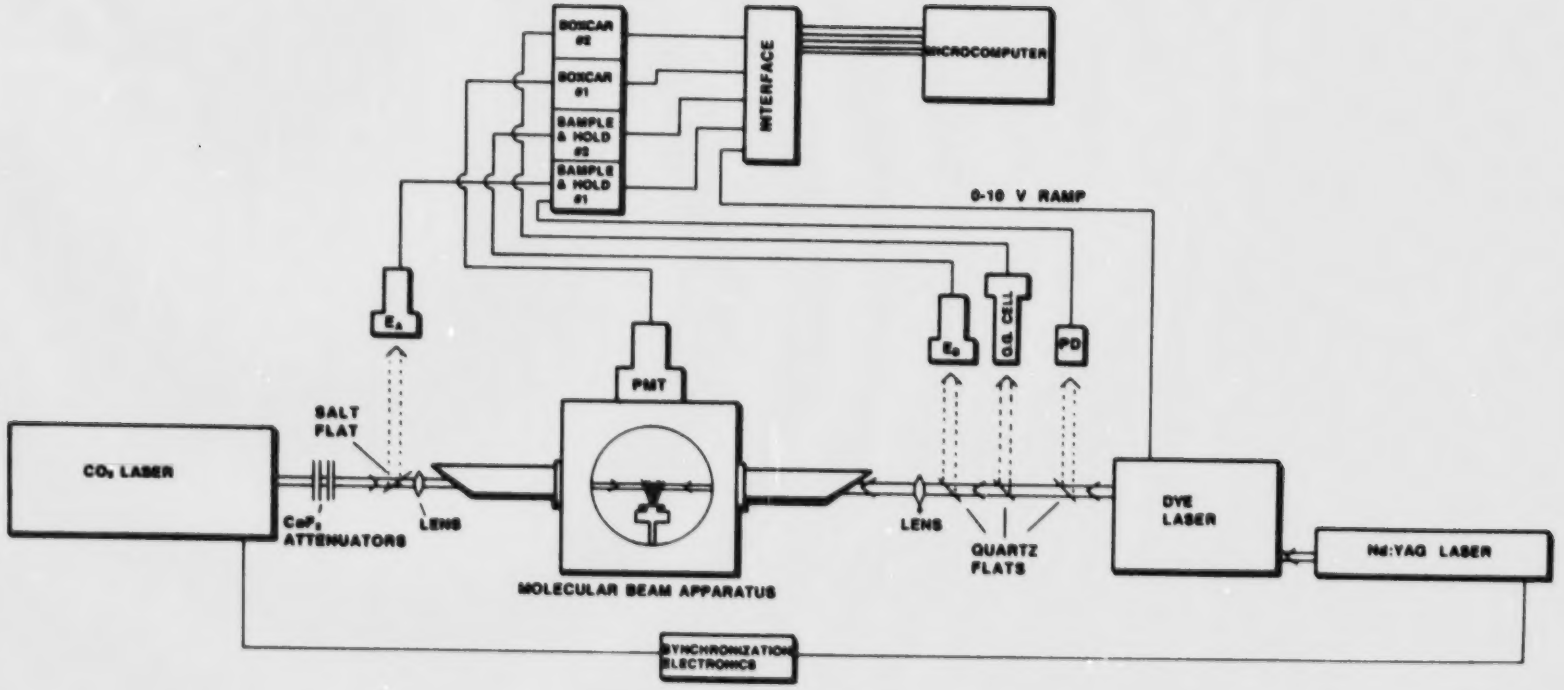
↓

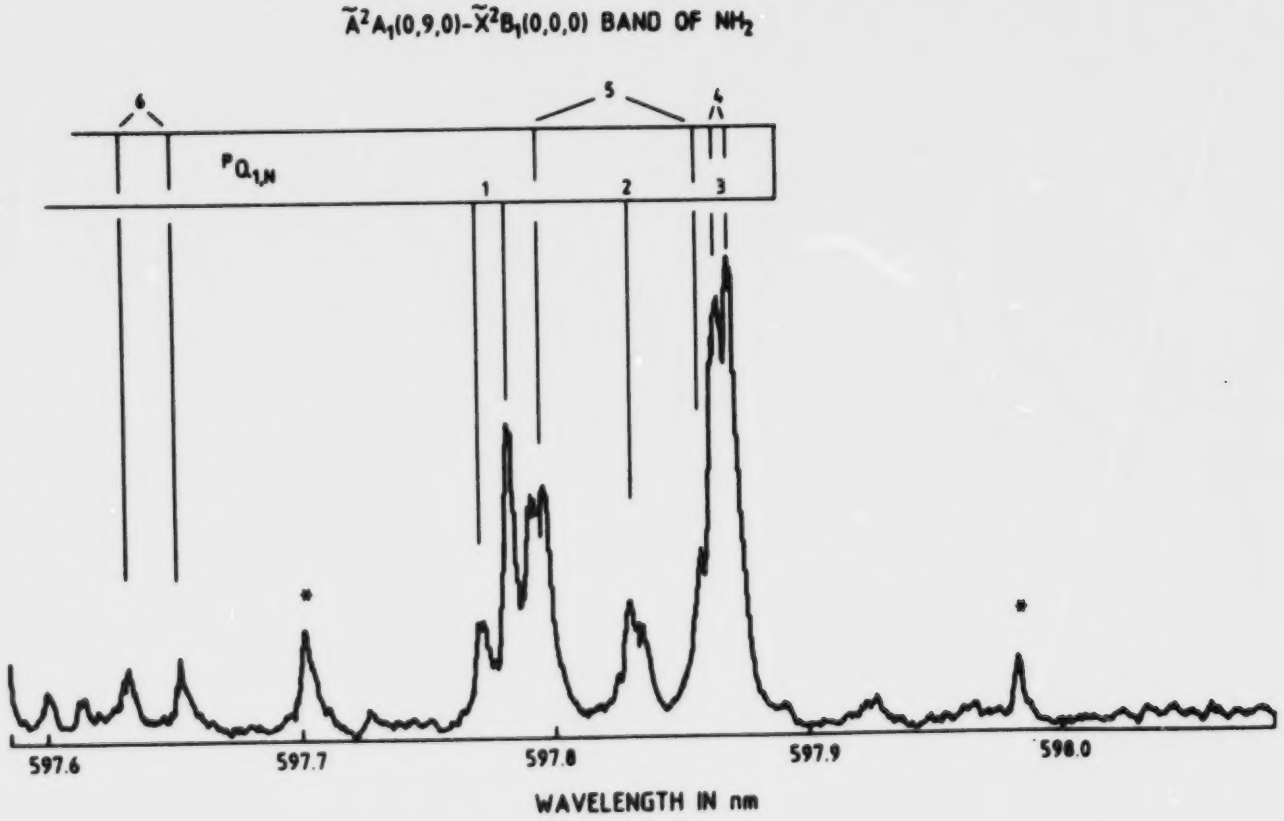
SHORT LIST (22)

↓

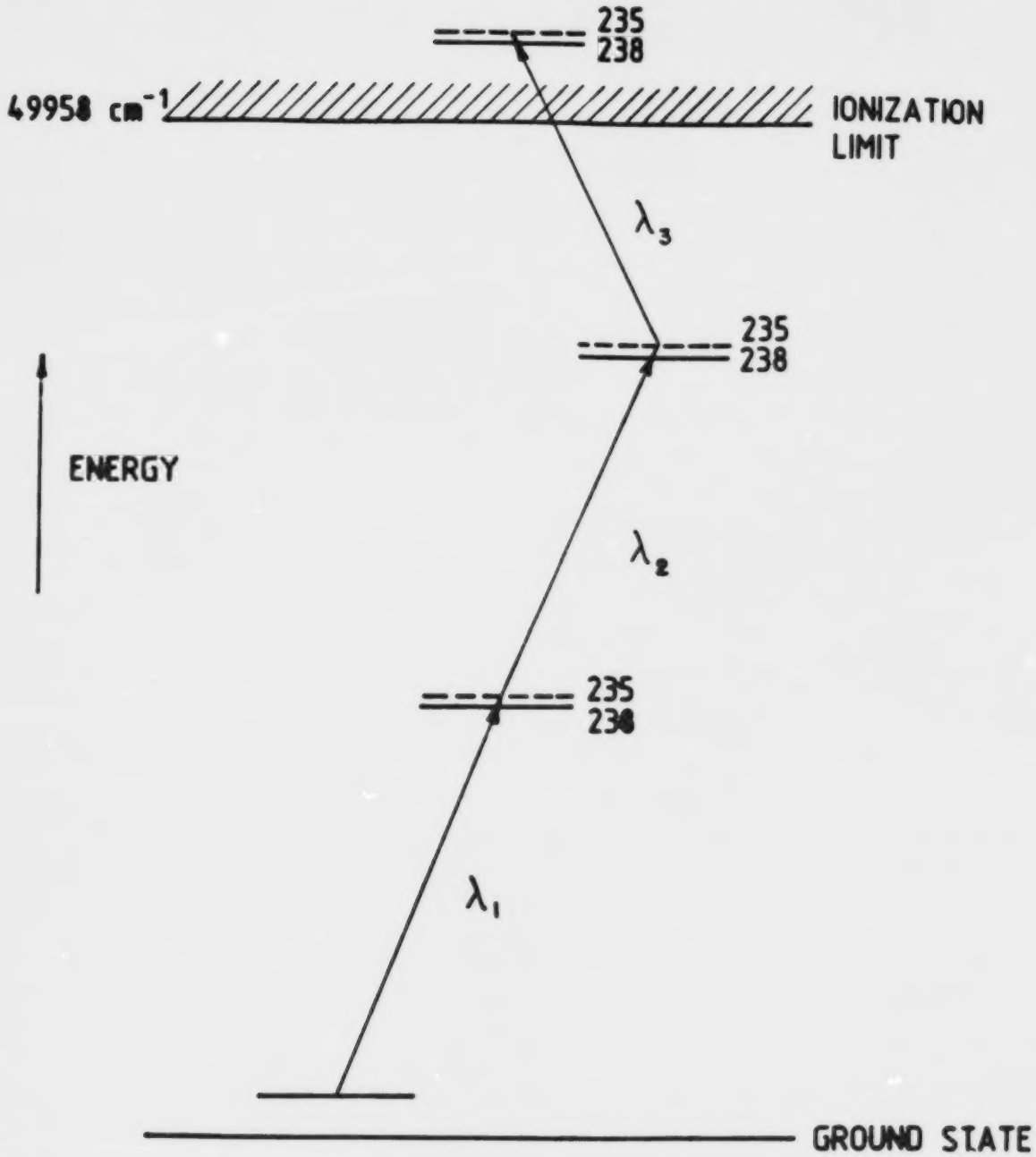
FINAL CANDIDATES (1-3)

EXPERIMENTAL SET-UP

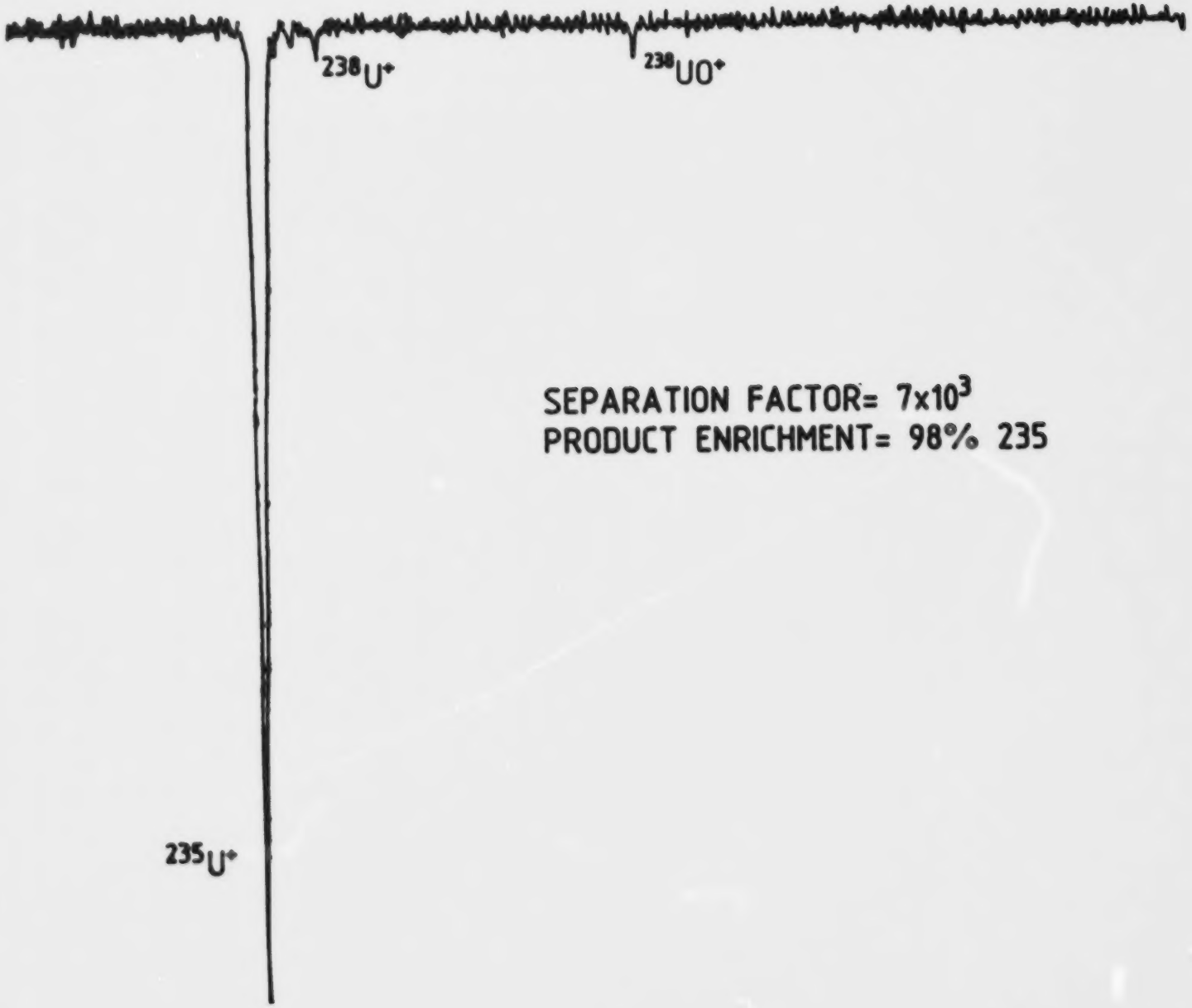



$\tilde{A}^2A_1(0,9,0)$-$\tilde{X}^2B_1(0,0,0)$ BAND OF NH_2
6
5
4
$^PQ_{1,N}$
1
2
3
*
*
597.6
597.7
597.8
597.9
598.0
WAVELENGTH IN nm

ISOTOPICALLY SELECTIVE RESONANCE IONIZATION OF URANIUM



VAPOUR

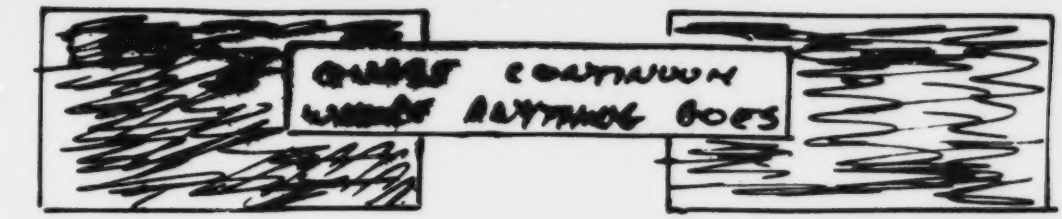


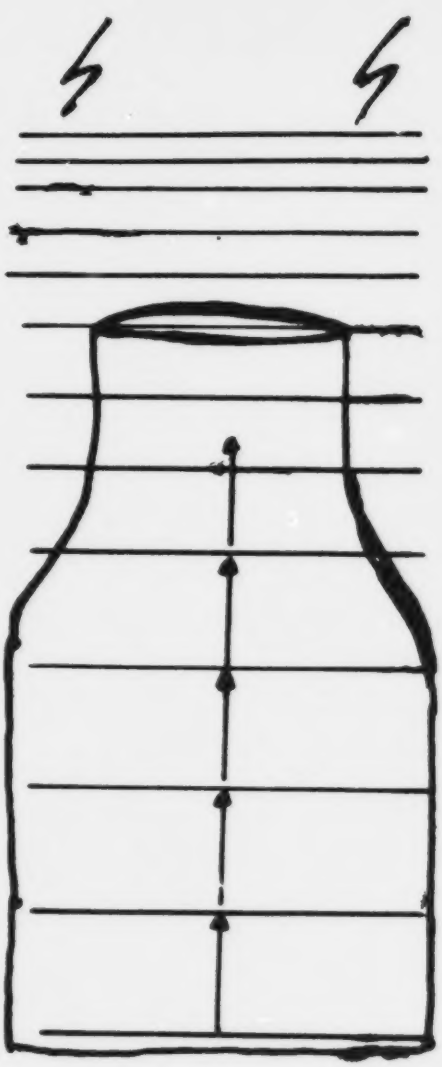
SEPARATION FACTOR= 7×10^3
PRODUCT ENRICHMENT= 98% 235

89-49

TWO-COLOUR $^{13}CO_2$ MULTIPHOTON ABSORPTION OF $CDCl_3$

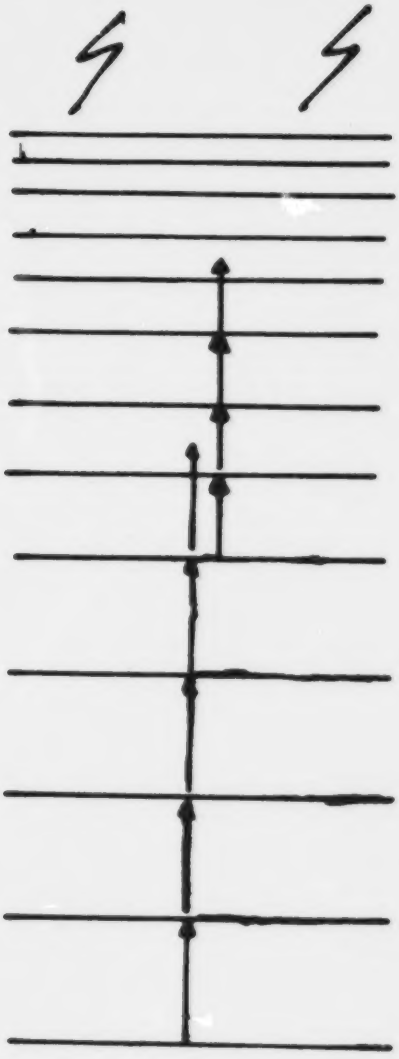
G. McRae
Chalk River Nuclear Laboratories
Chalk River, Ontario, K0J 1J0



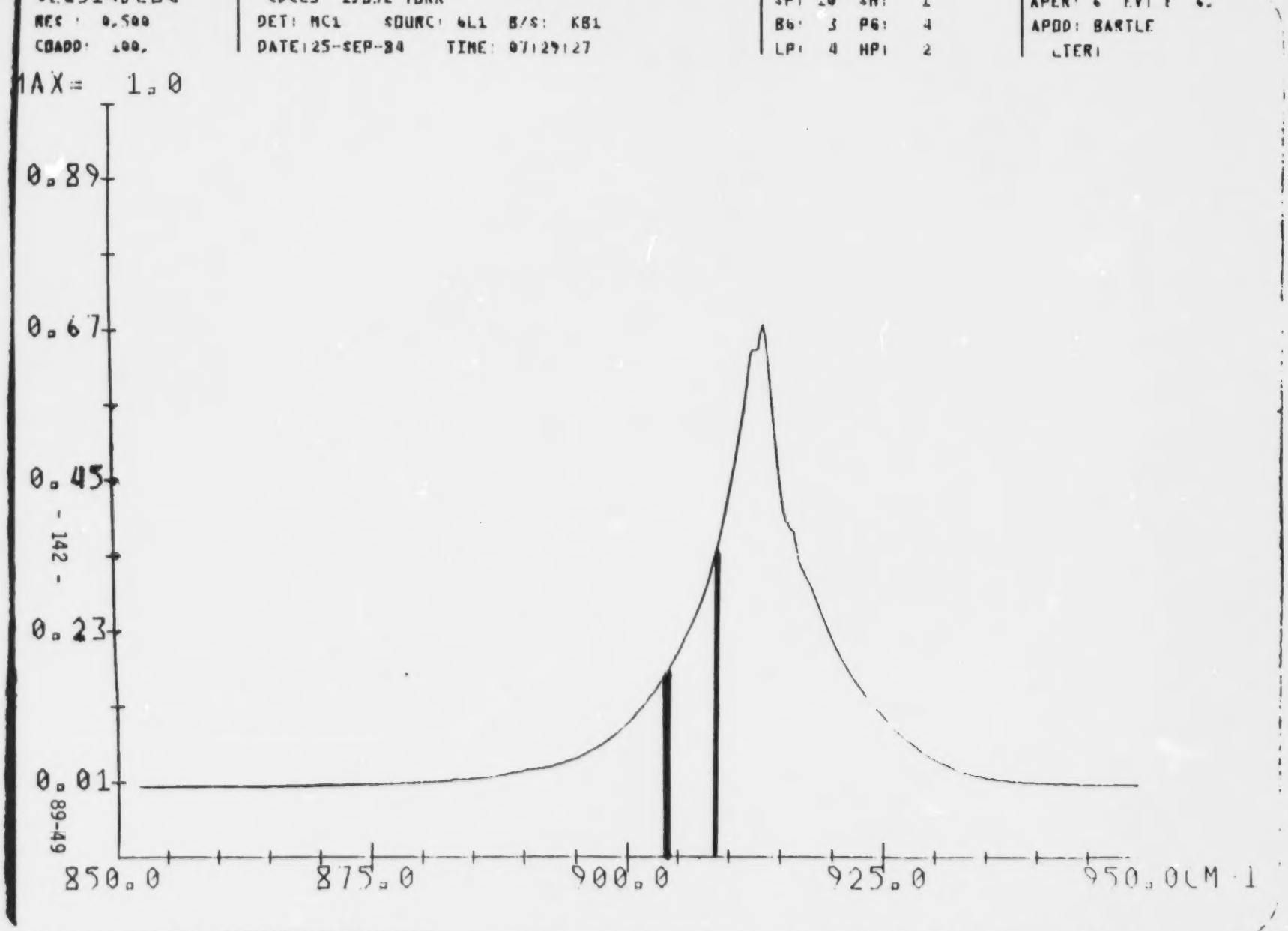


BOTTLE NECK FOR THE BLUE

→ CAN BE OVERCOME AT HIGHER FLUENCE



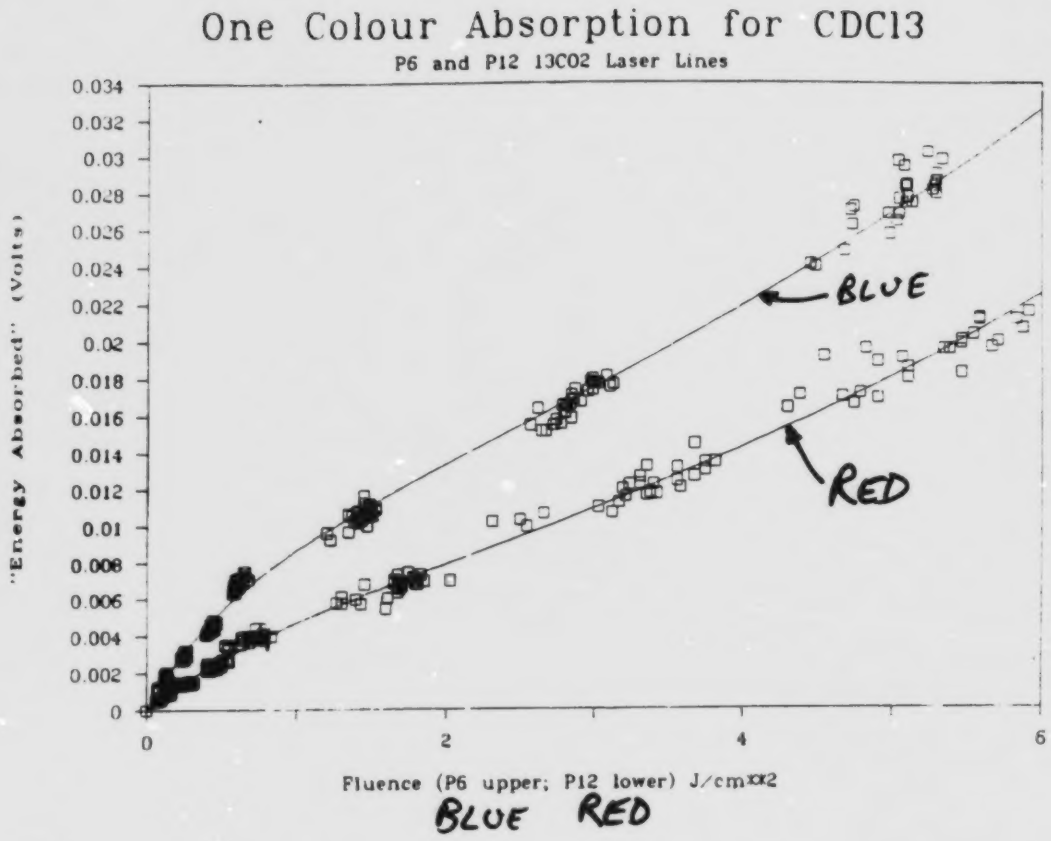
BLUE BOTTLENECK OVERCOME WITH A SECOND RED SHIFTED LASER


SE2514.LOG
RES : 0.500
CDADD: 100.
CDCL3 1.852 TORR
DET: MC1 SOURC: 6L1 B/S: KB1
DATE:25-SEP-84 TIME: 07:29:27
SP: 20 SM: 1
BG: 3 PG: 4
LP: 4 HP: 2
APER: 6 FV: F 6.
APOD: BARTLE
ITER:
MAX= 1.0
0.89
0.67
0.45
0.23
0.01
850.0
875.0
900.0
925.0
950.0
CM-1

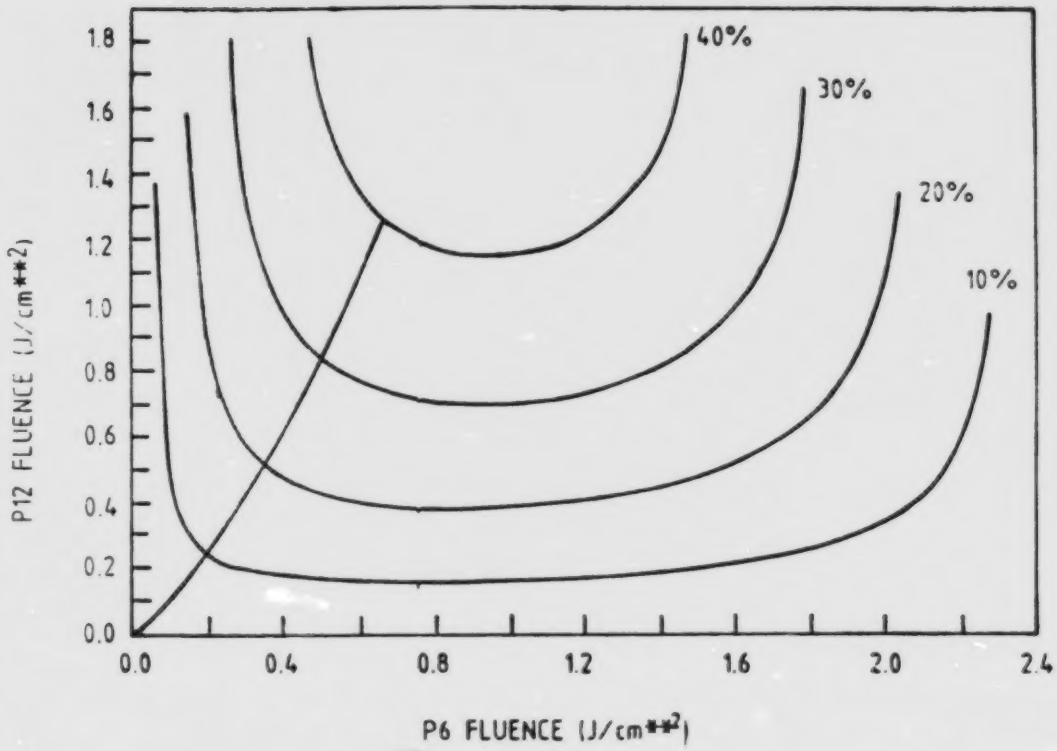
89-49

DUAL BEAM LASER:
OPTICAL SET-UP

89-49


One Colour Absorption for CDC13
P6 and P12 13C02 Laser Lines
"Energy Absorbed" (Volts)
0.034
0.032
0.03
0.028
0.026
0.024
0.022
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
2
4
6
BLUE
RED
Fluence (P6 upper; P12 lower) J/cmxx2
BLUE RED

TWO COLOUR ENHANCEMENT CONTOURS
CDC13



RED

BLUE

TRITIUM SEPARATION BY LASER

F.E. Bartoszek, K.E. Donnelly, K.M. Kalyanam, O.K. Kveton,
H.D. Morrison, J.A. O'Neill, J.R. Robins, S.K. Sood and K.B. Woodall

Ontario Hydro Research Division

Ontario Hydro Research Division has been developing a laser-based hydrogen isotope separation system (slides 2 and 3). We have recently produced a conceptual design of a large-scale system, and have compared it with eight combinations of conventional technology. The comparison reveals that laser-based tritium separation is competitive and cannot be ignored. The design is based on a requirement to process 500 kg/h of light water initially at 10 Ci/kg down to 1 Ci/kg, removing about 0.5 g/h of tritium. This requirement is representative of a system for tritium production from an aqueous lithium salt shield needed, for example, by the Next European Torus (NET). In terms of mass throughput and tritium extraction, this design is about 1.4 times as large as Ontario Hydro's Tritium Extraction Facility at Darlington, which is the largest system today. At this time we are concentrating on the separation of tritium from light water. The technique, however, can be adapted for the separation of tritium from heavy water.

The laser-based separation system consists of four parts. In the first part, a catalytic exchange process transfers the tritium from the feed water to a process gas, trifluoromethane. Then, the gas passes to a cell where the tritiated component is dissociated on exposure to high energy fluence pulses from a carbon dioxide laser. The third part of the system captures the product of the laser dissociation, tritium fluoride, and then converts it to hydrogen gas (slides 4 and 5). An optimized design for this separation process (slide 6) produces a mixture of about 3% tritium in hydrogen. Final enrichment of the tritium is performed by cryogenic distillation (slide 7).

The basic research to understand the exchange and separator components of the process is essentially complete. The next step is to test a pilot plant with these components (slides 8, 9 and 10). Fundamental research continues into laser dissociation of tritiated trifluoromethane to determine the essential design requirements of the dissociation cell and of the laser system. Research into cryogenic distillation of hydrogen gas is already at the pilot plant stage, including the demonstration of an inexpensive, compact, high power cooler that employs a helium compressor rather than liquid helium or liquid hydrogen.

Comparison of the design for the laser-based separation system with the designs for eight conventional processes was based on capital cost (slide 11). Our estimates for all these processes show that the laser-based design has a capital cost about half that of the least expensive alternatives. Thus, laser-based tritium separation is clearly competitive. Development of the process into the pilot plant stage is continuing and may reduce the costs further.

Slide 1

LASER-BASED HYDROGEN ISOTOPE SEPARATION SYSTEM FOR LARGE-SCALE APPLICATIONS*

F.E. Bartoszek, K.E. Donnelly, K.M. Kalyanam, O.K. Kveton,
H.D. Morrison, J.A. O'Neill, J.R. Robins, S.K. Sood, K.B. Woodall

Ontario Hydro
Toronto, Ontario, Canada

*This work supported in part by the Canadian Fusion Fuels Technology Project.

Slide 2

LASER ISOTOPE SEPARATION

- Dissociation of molecules by absorption of light
- Isotopically selective
- Yields easily separated products

Slide 3

LASER ISOTOPE SEPARATION PLANT

- Incorporates laser process in a closed gas loop
- Feed stream replenishes depleted isotope in gas stream by chemical exchange
- Gas clean-up removes product

Slide 4

PROCESS STEPS

- Tritium in water transfers to CF_3H

  $HTO + CF_3H \rightarrow CF_3T + H_2O$

- CO_2 laser selectively dissociates CF_3T

  $2CF_3T \rightarrow 2TF + C_2F_4$

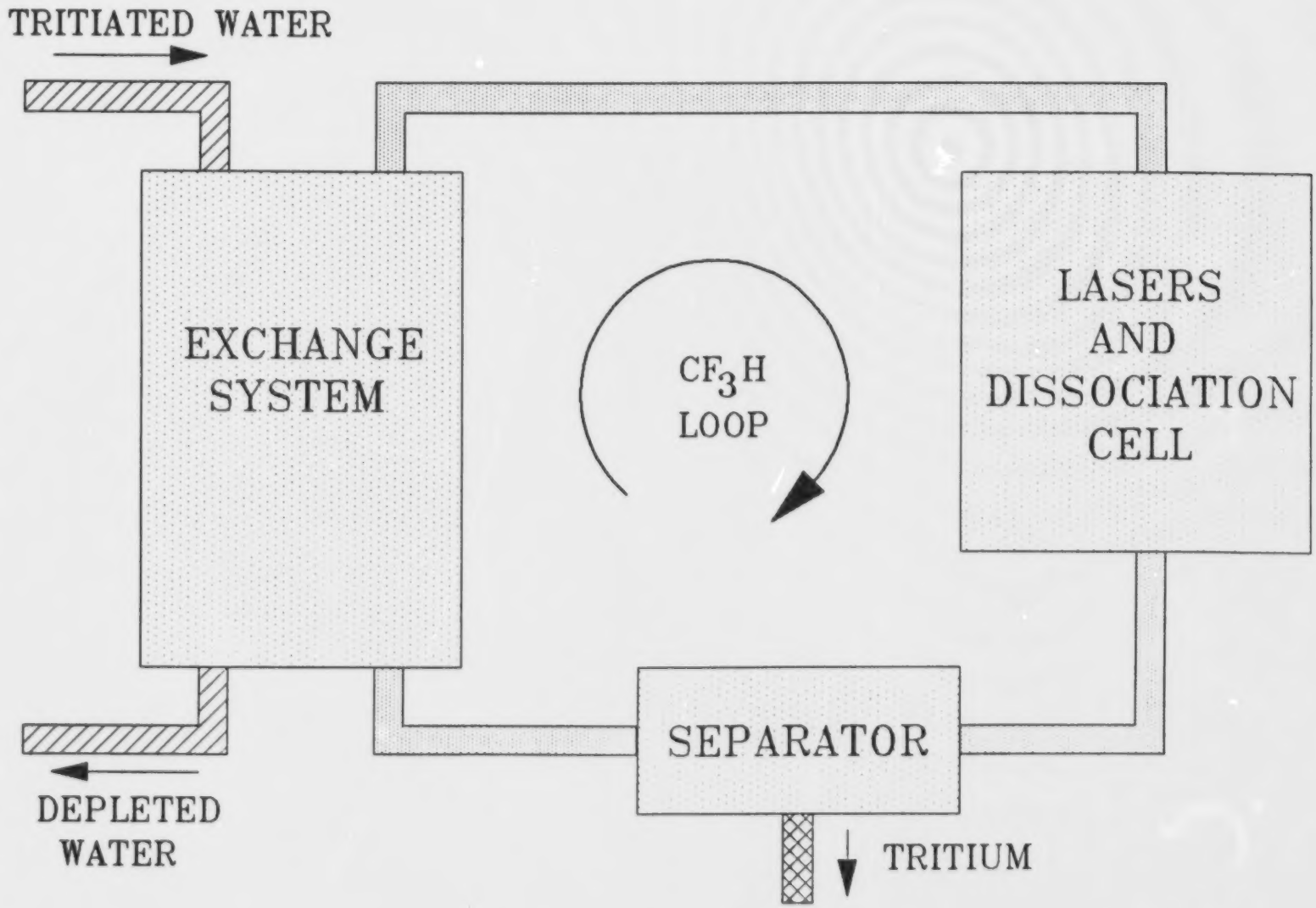
- TF product captured on NaF beds

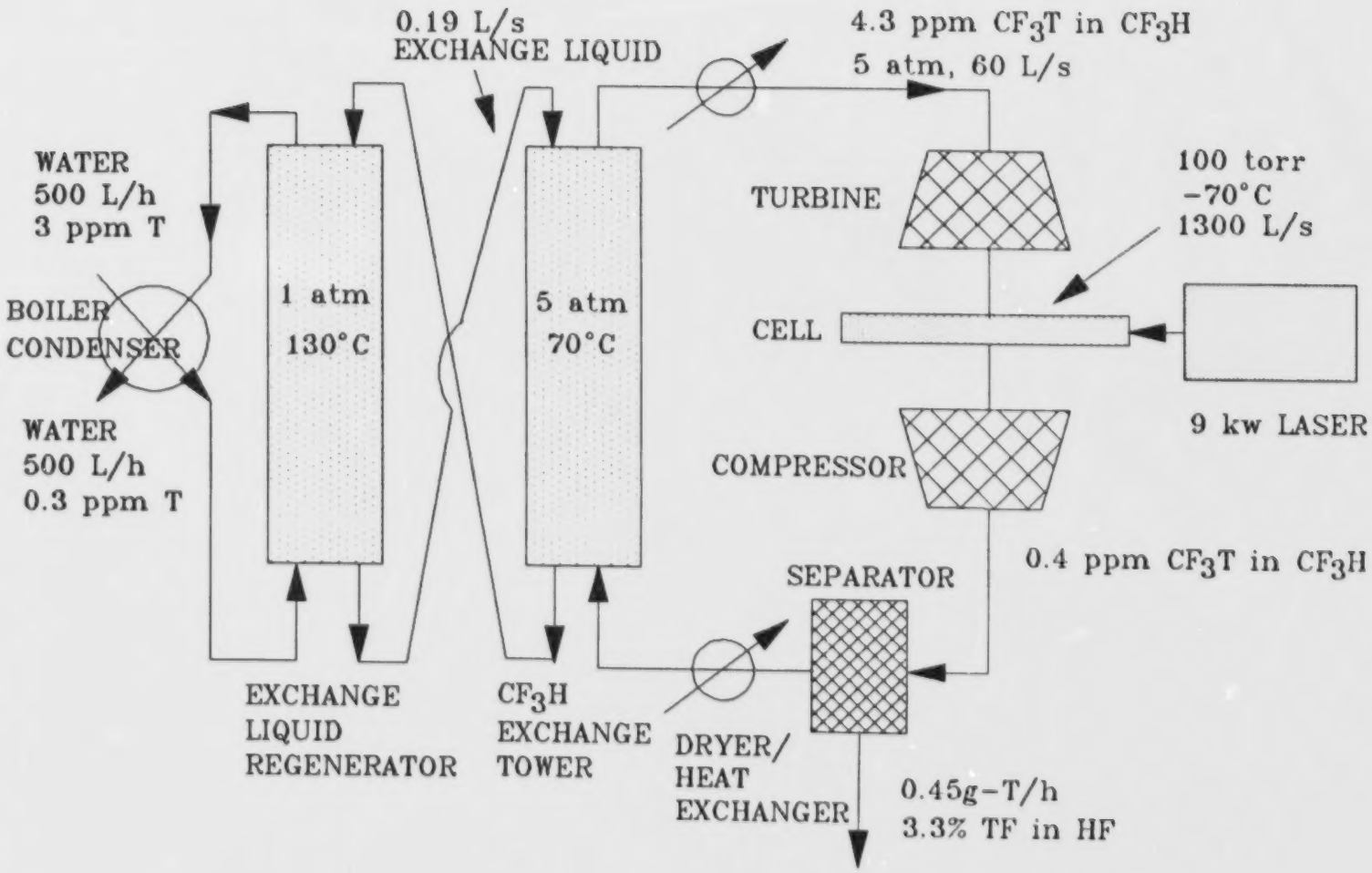
  $TF + NaF \rightarrow NaTF_2$

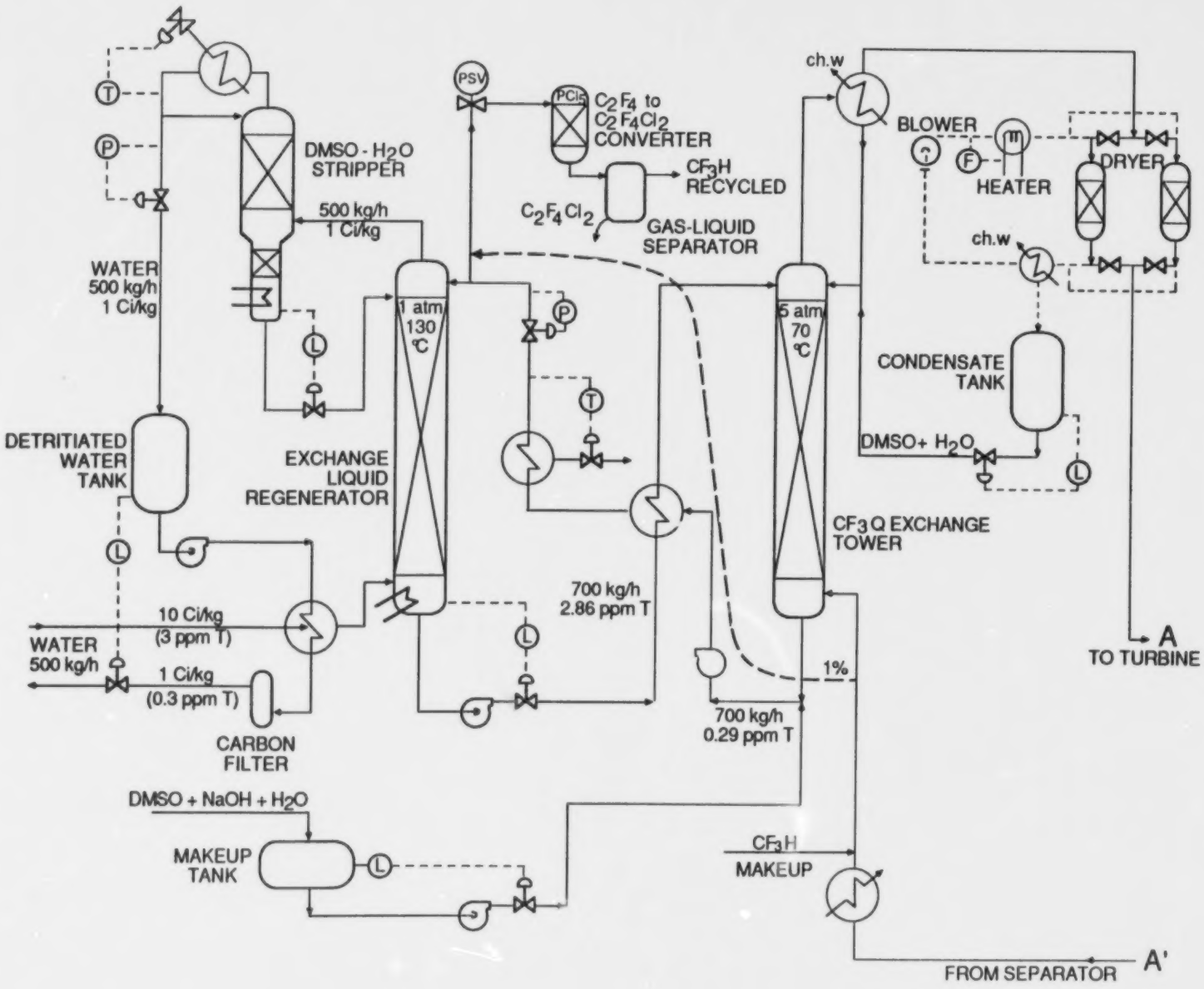
Slide 6

DESIGN SPECIFICATIONS

- 500 kg/hr tritiated water
- Input concentration 10 Ci/kg (3 ppm T in H)
- Output concentration 1 Ci/kg

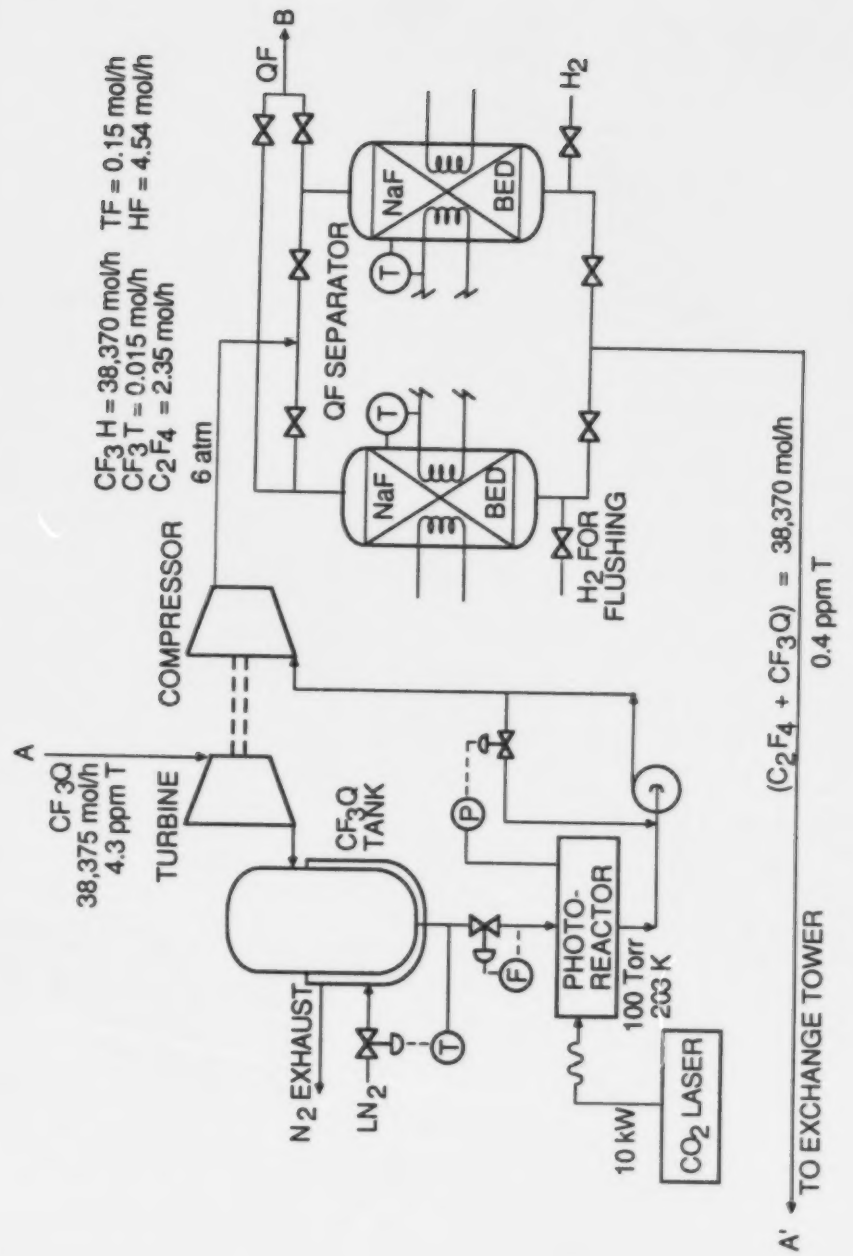

TRITIATED WATER
EXCHANGE SYSTEM
CF_3H LOOP
LASERS AND DISSOCIATION CELL
SEPARATOR
DEPLETED WATER
TRITIUM


0.19 L/s
EXCHANGE LIQUID
4.3 ppm CF_3T in CF_3H
5 atm, 60 L/s
WATER
500 L/h
3 ppm T
TURBINE
100 torr
−70°C
1300 L/s
BOILER
CONDENSER
1 atm
130°C
5 atm
70°C
CELL
9 kw LASER
WATER
500 L/h
0.3 ppm T
COMPRESSOR
0.4 ppm CF_3T in CF_3H
SEPARATOR
EXCHANGE
LIQUID
REGENERATOR
CF_3H
EXCHANGE
TOWER
DRYER/
HEAT
EXCHANGER
0.45g−T/h
3.3% TF in HF


T
P
DMSO - H_2O STRIPPER
500 kg/h
1 Ci/kg
WATER
500 kg/h
1 Ci/kg
L
1 atm
130 °C
PSV
PCIs
C_2F_4 to $C_2F_4Cl_2$ CONVERTER
CF_3H RECYCLED
$C_2F_4Cl_2$
GAS-LIQUID SEPARATOR
ch.w
BLOWER
F
HEATER
DRYER
5 atm
70 °C
CONDENSATE TANK
DMSO+ H_2O
DETRITIATED WATER TANK
EXCHANGE LIQUID REGENERATOR
CF_3Q EXCHANGE TOWER
700 kg/h
2.86 ppm T
10 Ci/kg
(3 ppm T)
WATER
500 kg/h
1 Ci/kg
(0.3 ppm T)
CARBON FILTER
1%
700 kg/h
0.29 ppm T
A
TO TURBINE
DMSO + NaOH + H_2O
MAKEUP TANK
CF_3H
MAKEUP
A'
FROM SEPARATOR

Slide 8

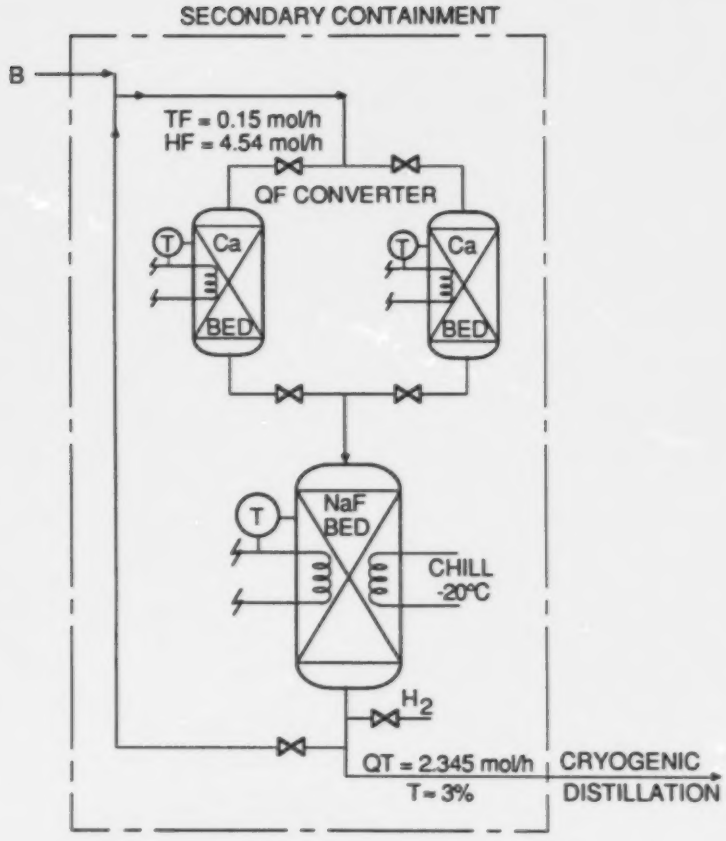
Slide 9



89-49

608.607 45%
CAZ-4

Slide 10


SECONDARY CONTAINMENT
B
TF = 0.15 mol/h
HF = 4.54 mol/h
QF CONVERTER
T
Ca
BED
T
Ca
BED
T
NaF
BED
CHILL
-20°C
H_2
QT = 2.345 mol/h
T = 3%
CRYOGENIC
DISTILLATION

Slide 11

ISOTOPE SEPARATION SYSTEMS

Process 500 kg/h					Total Capital Cost ($CAN Millions)	Energy Use MW Thermal	MW Electric
		VPCE	+	CD	35.2	--	2
DW	+	VPCE	+	CD	26.4	11	0.7
2DW	+	VPCE	+	CD	25.3	12	0.1
DW	+	LPCE	+	CD	27.1	12	1.1
2DW	+	LPCE	+	CD	22.7	12	0.1
DW	+	CECE	+	CD	23.5	11	0.6
DW	+	E	+	CD	22.7	11	0.6
		E	+	CD	22	--	2
		LIS	+	CD	11.7	0.4	0.2

SEPARATION OF SILICON, SULFUR, CHLORINE, AND SELENIUM ISOTOPES BY DISTILLATION

Thomas R. Mills, Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545

INTRODUCTION

Stable isotopes of most elements can be separated electromagnetically by calutrons, but production quantities are usually measured in milligrams, and the resulting costs are high. Until alternate separation techiques are developed, some applications for stable isotopes will be limited by availability and costs. For example, distillation separation processes for isotopes of carbon, nitrogen, and oxygen have greatly increased availability and lowered costs for these isotopes relative to those of previous processes. As a result, the fields of biomedicine and agriculture now use enriched heavy isotopes of C, N, and O at about the 10 kg/yr level each.

Because of previous successes and because it is a process which easily lends itself to scaleup, distillation is worthy of consideration in seeking new isotopic separation processes. Isotopic separations have been sought in recent work for silicon, sulfur, chlorine, and selenium. While it is important to have potential applications for the separated isotopes in mind (e.g. S for acid rain, Se for radioisotope production), many isotope applications have been developed only after researchers were aware the enriched isotopes were available at low cost.

EXPERIMENTAL

Three different packed distillation columns were used for experiments. Stainless steel wire helices (Heli-Pak) of different sizes was used for the packing. Each column was housed in a vacuum jacket and was wrapped with multiple layers of aluminized mylar for thermal insulation. The temperature of the columns was controlled by using a heat pipe condenser or by using a helium refrigerator. The heat pipe fluid used was an equimolar mixture of ethane and propane. Column details are summarized in Table 1. Figure 1 gives a schematic diagram of Column 3.

Each time the compound distilled was changed, the packing was preflooded with liquid to obtain the maximum number of separating stages. The column was then deflooded until minimal bulk liquid remained in the packing, as monitored by pressure drop through the packing. The column was allowed to reflux without drawoffs, and samples were collected until steady state concentration were observed in samples of top and bottom gas.

All gas samples were analyzed for isotopic composition without conversion to other chemical forms. Isotopic analyses were done on a CEC 21-621 cycloidal mass spectrometer and on Nuclide 6-60-RMS and 12-90-GQ

magnetic sector mass spectrometers. Column top and bottom samples were analyzed in pairs to obtain the overall column isotopic separation.

The isotopic separations were computed from mass spectrometer data in different ways for the various compounds. The isotopic ratios in SF_4 were calculated directly from the SF_3^+ peaks, as fluorine is monisotopic. Likewise, the isotopic ratios in SiF_4 were calculated from the SiF_3^+ peaks. Fragmention peaks of S^+ and HS^+ are observed when analyzing H_2S, but the fragmentation pattern relative to H_2S^+ is invarient with isotopic substitution. Accordingly, the ratio of $^{32}S^+/H_2{}^{34}S^+$ for column top and bottom samples was used to obtain the separation. For COS, the S^+ fragments were used to obtain the sulfur isotope separation, and the C^+ fragments were used for carbon isotopes. Both carbon isotopic peaks and a typical hydrocarbon fragmentation pattern complicate the isotopic analysis of CH_3SH. The peaks CH_xS^+ (x = 0 to 4) were used. First adjustments were made to allow for the natural abundance of 1.1% ^{13}C, then the data were fitted by least squares assuming fragmentation patterns to be isotope invarient. Parent peaks of HCl and Cl_2 were used to measure chlorine isotopic separation in HCl and Cl_2.

RESULTS

Four sulfur compounds were distilled in Columns 1-3. The chlorine and silicon compounds were studied only in column 3. Total isotope separations are given in Table 2 and Figures 2-7.

In H_2S, COS, CH_3SH, HCl, and Cl_2, the higher mass isotopes are less volatile. This effect is normally expected. A sizeable inverse isotope effect was found for SF_4 and SiF_4. The separations for different isotopic species in SF_4, SiF_4, COS, and Cl_2 followed the expected pattern, with α-1 proportional to the isotopic mass difference. Isotopic separations in SF_4 and HCl showed a definite temperature dependence. Temperature dependence of other separations was either absent or unclear.

In addition to the sulfur isotope separation, a reverse carbon isotope separation was found in COS. The carbon isotopes are separated more strongly than sulfur isotopes in COS, and ^{13}C tends to go the column top while ^{34}S tends to go to the bottom.

To obtain an estimate of the number of theoretical plates, CO was distilled in Column 3, and the isotopic separations were measured. The number of theoretical plates in Column 3 was 80 if one uses the ^{13}C data and 64 if one uses the ^{18}O data. The expected HETP for medium sized Heli-Pak with CO is 2.0 cm. Using this result, Column 3 has 75 theoretical plates, and the inferred relative volatility, α, for each compound is given in Table 3. Plate height is not necessarily the same for different compounds on a particular packing, thus these numbers must bear that qualification.

Dimethyl selenide ($(CH_3)_2Se$) was distilled in Column 1, and H_2Se was distilled in Column 2. Analysis of the data was greatly complicated by the combination of six selenium isotopes and the mass spectrometer fragmentation patterns. The $(CH_3)_2Se$ data was treated by a least square fit with the assumption of isotope invarient fragmentation pattern, and essentially no isotope separation was observed. A calculated upper limit of relative volatility of 1.00001 per mass unit difference could be accomodated by the fit of the data.

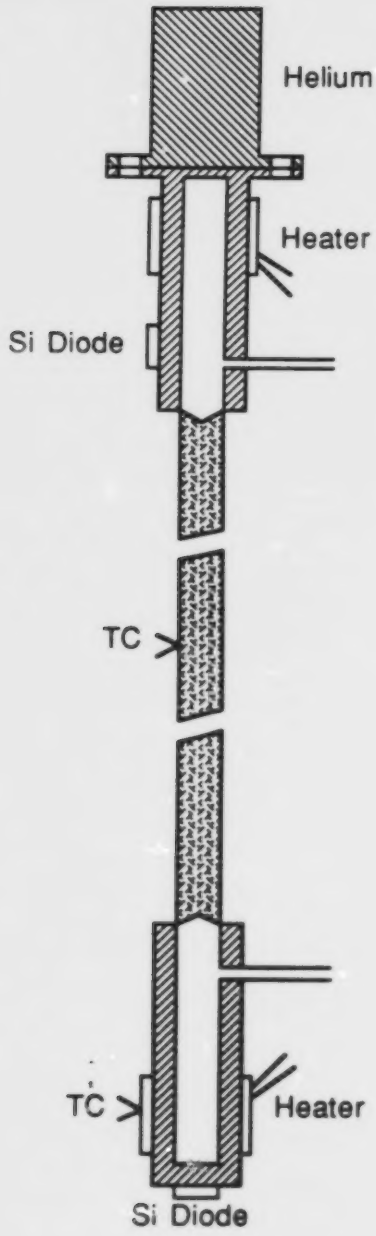
Very limited data was collected for H_2Se, but it appears that there is an isotope effect, and the higher mass isotopes are less volatile. The ratio of the 78/82 m/e peaks from the column top was 1.02 times this ratio for the column botom gas. Other low/high m/e peak ratios were also larger at the top of the column. This indicates the lower mass selenium isotopes concentrate at the column top.

DISCUSSION

The sulfur and silicon isotope separations in SF_4 and SiF_4 are exciting, for both magnitude and reverse nature. These isotope effects are about one-fourth of the $^{12}C/^{13}C$ separation in CO distillation, which is the standard means of producing ^{13}C. The reverse effects for SiF_4, SF_4, and COS have not previously been noted by others. While this effect is not predictable, in each case the reverse effect occurs for a central atom of a polyatomic compound where the total mass of the outlying atoms is notably greater than the central atom.

Additional silicon compounds will be investigated for possible isotopic separations. Hydrogen selenide shows some promise as a medium for selenium separation, and it will be studied further, along with other selenium compounds.

Based upon the isotope separation in SiF_4, SF_4, and H_2S, distillation is a practical means for silicon and sulfur isotope separation. The chlorine isotope effect in HCl is also large enough to be used for a practical separation. Many stages of separation would be required, but this has been demonstrated with existing isotope distillation technology.



EXPERIMENTAL ISOTOPE COLUMN

PACKED REGION 1.50 m by 14 mm i.d.
HELI-PAK 1.3 x 2.5 x 2.3 mm

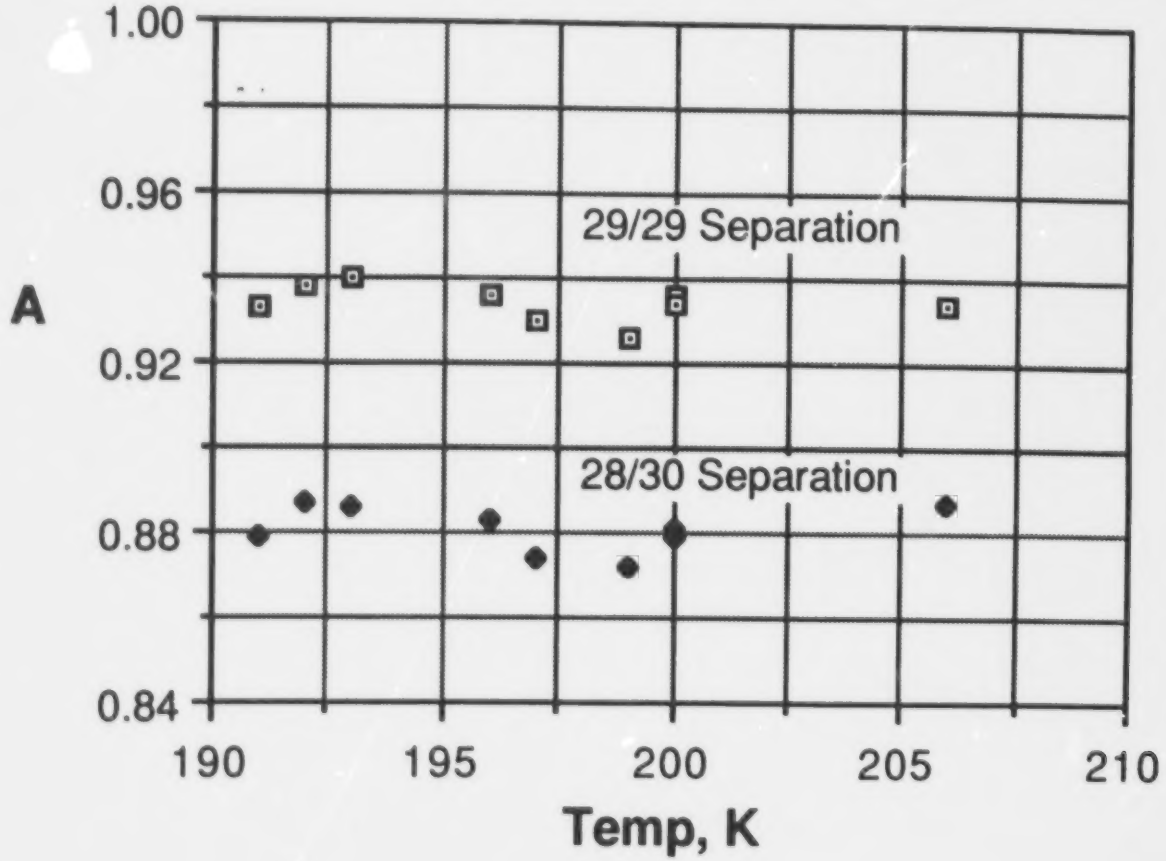
TABLE 1 DISTILLATION COLUMN DETAILS

Column	Condenser	Length	Diameter	Packing
1	Heat Pipe	107 cm	8 mm	0.8x1.8x1.7 mm
2	Heat Pipe	107 cm	14 mm	1.3x2.5x2.3 mm
3	Helium Refrig	150 cm	14 mm	1.3x2.5x2.3 mm

TABLE 2 TOTAL COLUMN $^{32}S/^{34}S$ SEPARATION

Compound	Column	Pressure	Separation	Spectrometer
SF_4	1	400 torr	0.865	21-621
	1	820	0.922	21-621
	3	660	0.838	12-90-GQ
H_2S	2	300	1.127	21-621
COS	2	700-800	1.031	21-621
	3	550	1.048	21-621
	3	1050	1.037	21-621
CH_3SH	2	240	1.058	6-60-RMS

TOTAL ISOTOPE SEPARATION IN SiF4



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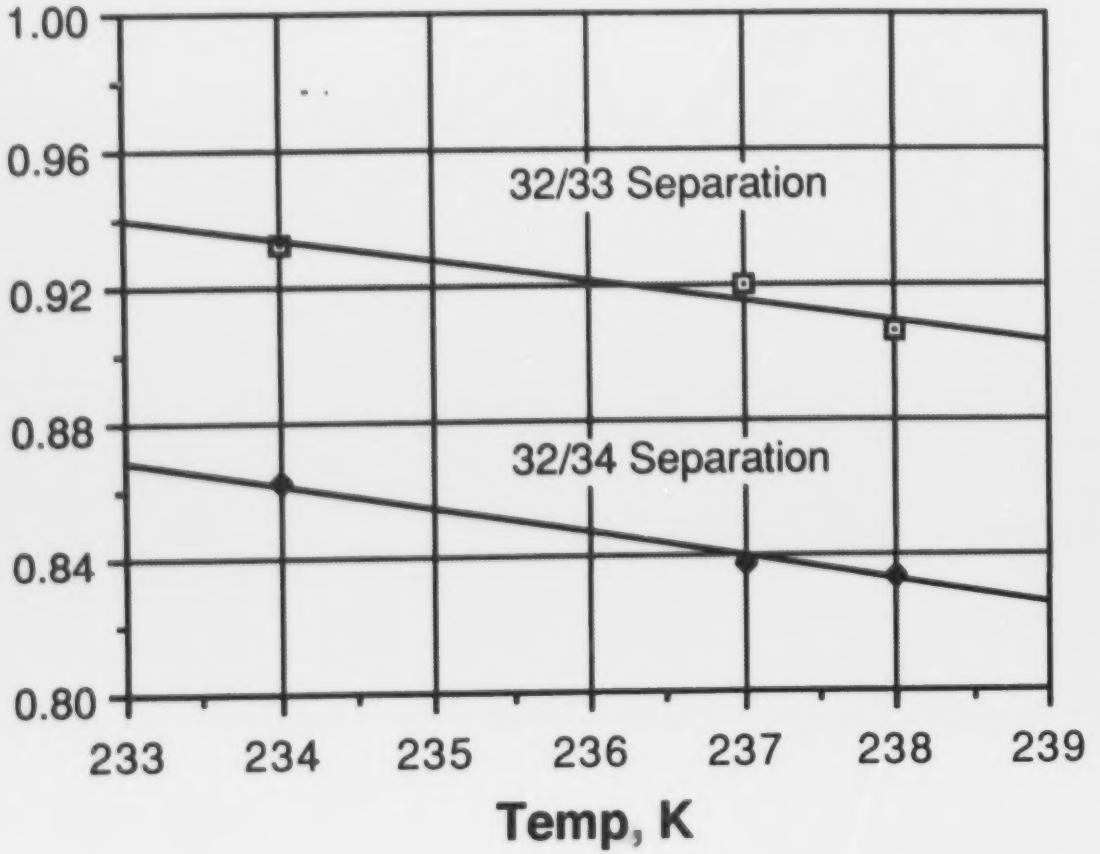
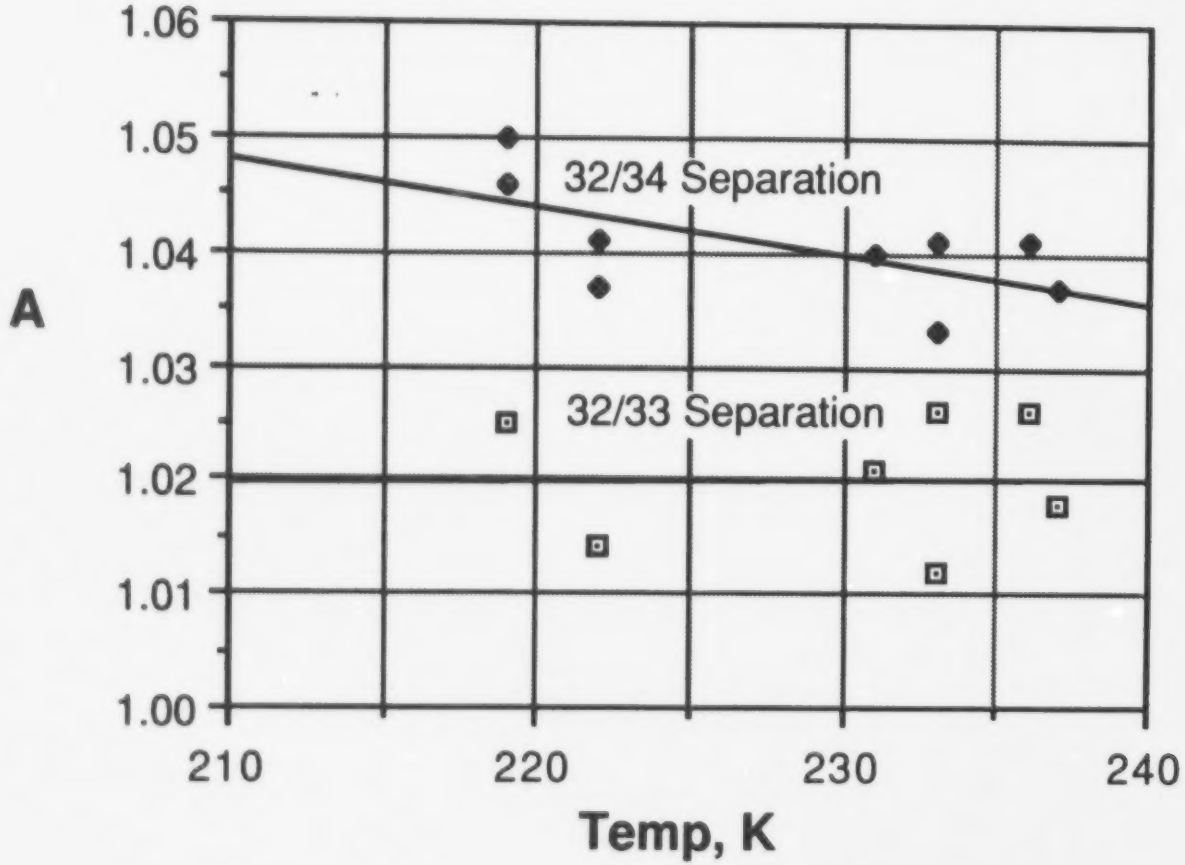
TOTAL ISOTOPE SEPARATION IN SF4



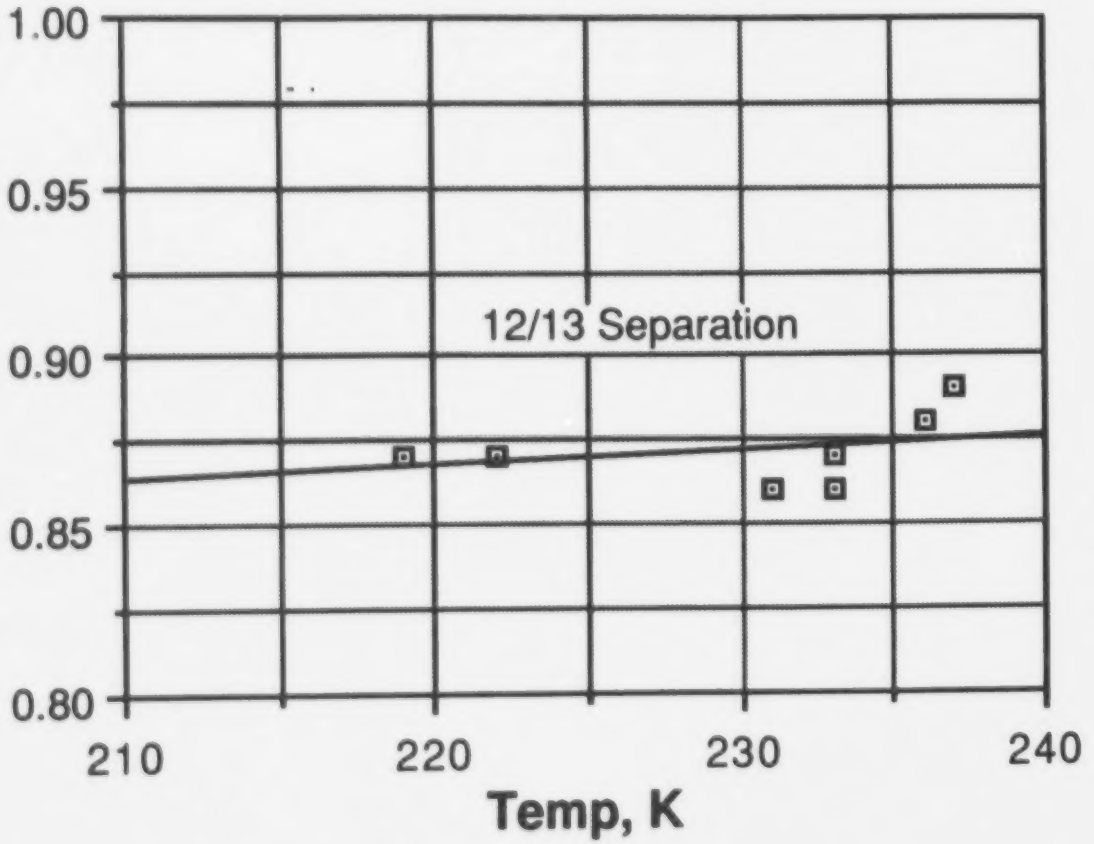
89-49

TOTAL ISOTOPE SEPARATION IN COS

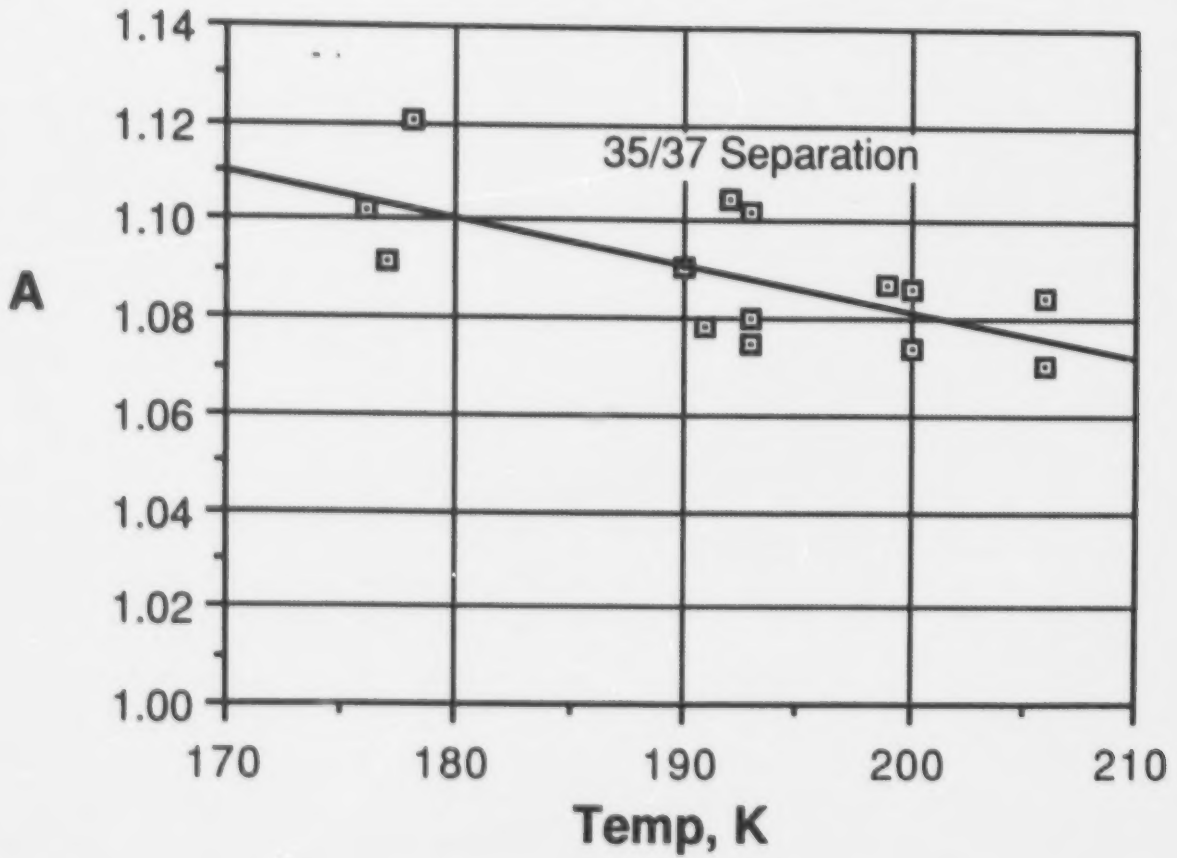


89-49

TOTAL ISOTOPE SEPARATION IN COS



TOTAL ISOTOPE SEPARATION IN HCl



TOTAL ISOTOPE SEPARATION IN CL2

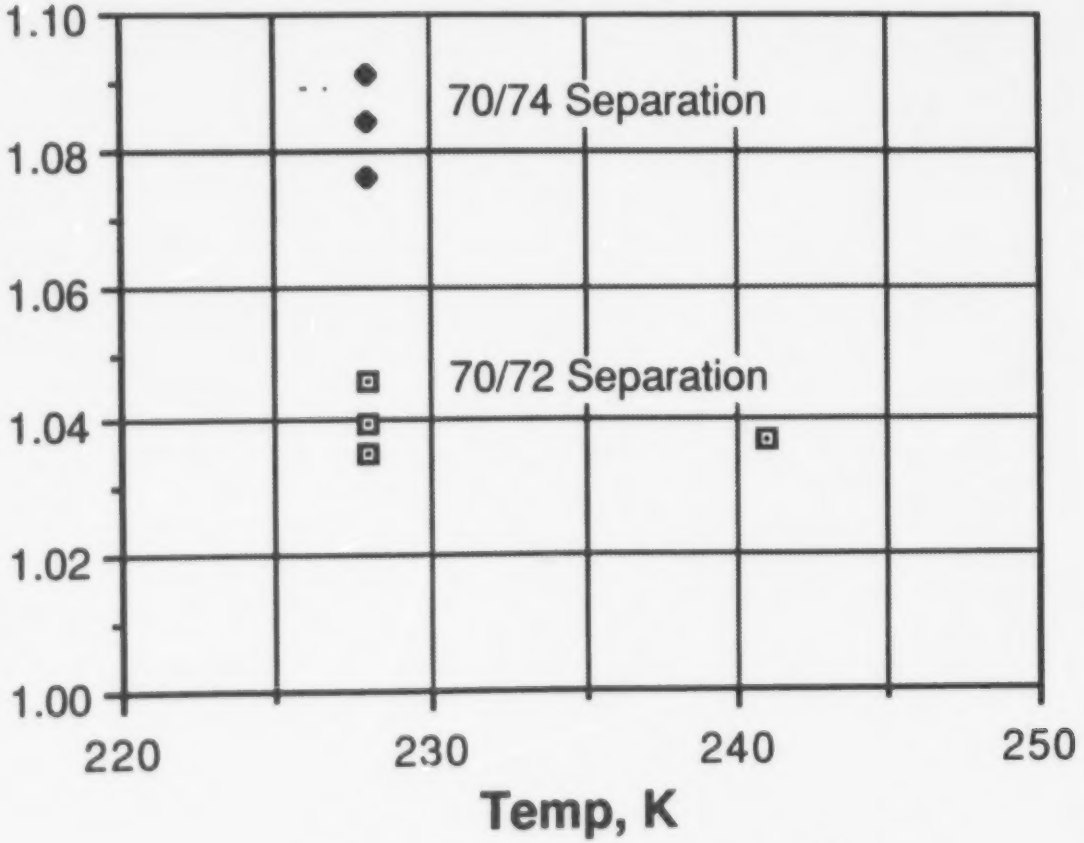


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TABLE 3. INFERRED RELATIVE VOLATILITIES

Compound	Isotopes	Temperatures	Relative Volatility
SiF_4	$^{28}Si/^{29}Si$ $^{28}Si/^{30}Si$	191 - 206 K	0.9990 - 0.9992 0.9982 - 0.9984
SF_4	$^{32}S/^{33}S$ $^{32}S/^{34}S$	234 - 238	0.9987 - 0.9991 0.9976 - 0.9980
COS	$^{32}S/^{33}S$ $^{32}S/^{34}S$ $^{12}C/^{13}C$	219 - 237	1.0002 - 1.0003 1.0004 - 1.0007 0.9980 - 0.9984
H_2S	$^{32}S/^{34}S$	196	1.0023
CH_3SH	$^{32}S/^{34}S$	254	1.0011
HCl	$^{35}Cl/^{37}Cl$	176 - 206	1.0009 - 1.0015
Cl_2	$^{35}Cl_2/^{35}Cl^{37}Cl$ $^{35}Cl_2/^{37}Cl_2$	228 - 241	1.0005 - 1.0006 1.0010 - 1.0012
H_2Se	Se isotopes	~230	~1.0001/Δm=1
$(CH_3)_2Se$	Se isotopes	~283	<1.00001/Δm=1

LOW-COST HYDROGEN ISOTOPE SEPARATION

K.B. Woodall, J.R. Robins, F.E. Bartoszek, D.G. Bellamy, R. Mowat
Ontario Hydro Research Division

LOW COST HYDROGEN ISOTOPE

CRYOGENIC DISTILLATION COLUMN

- Hydro Investment about $200 million
- Carbon isotope experience
- Research support and understanding of cryogenic distillation

- All Hydrogen stills cooled with liquid cryogens
- Hydrogen - Hydro and Grenoble (hazardous!!!)
- Helium - Everyone else (costly!!!)

LIQUID CRYOGENS

LIQUID	BOILING POINT K	MELTING POINT K	HEAT OF VAPORIZATION Joules/Mole
Helium	4.2	1.2	83.8
Hydrogen	20.4	13.95	899
Hydrogen Deuteride	22	16.3	1090
Deuterium	23.6	18.6	1220
Nitrogen	77.4	63.1	5578
Carbon Monoxide	81.6	68.1	6036

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Design of Research Still

- Wattage - CO Still (3/4 " column) - Floods at 72 W
  - Hydrogen Still should flood at 72*899/6036 = 10.7 W

- Experimental Result - 11 W ±1

Cooling Needed	11 W
Extra for Deuterium or Tritium	6 W
Losses	5 W
Contingency or bigger columns	8 W
Total	30 W

Helium Consumption

- Heat of Vaporization + Specific Heat - 224 Joules/mole
- 30 W = 2600 L/wk
- > $18000/wk
- $1 million/yr

- Helium recovery saves at least half
- Dewars cost $50 000 US

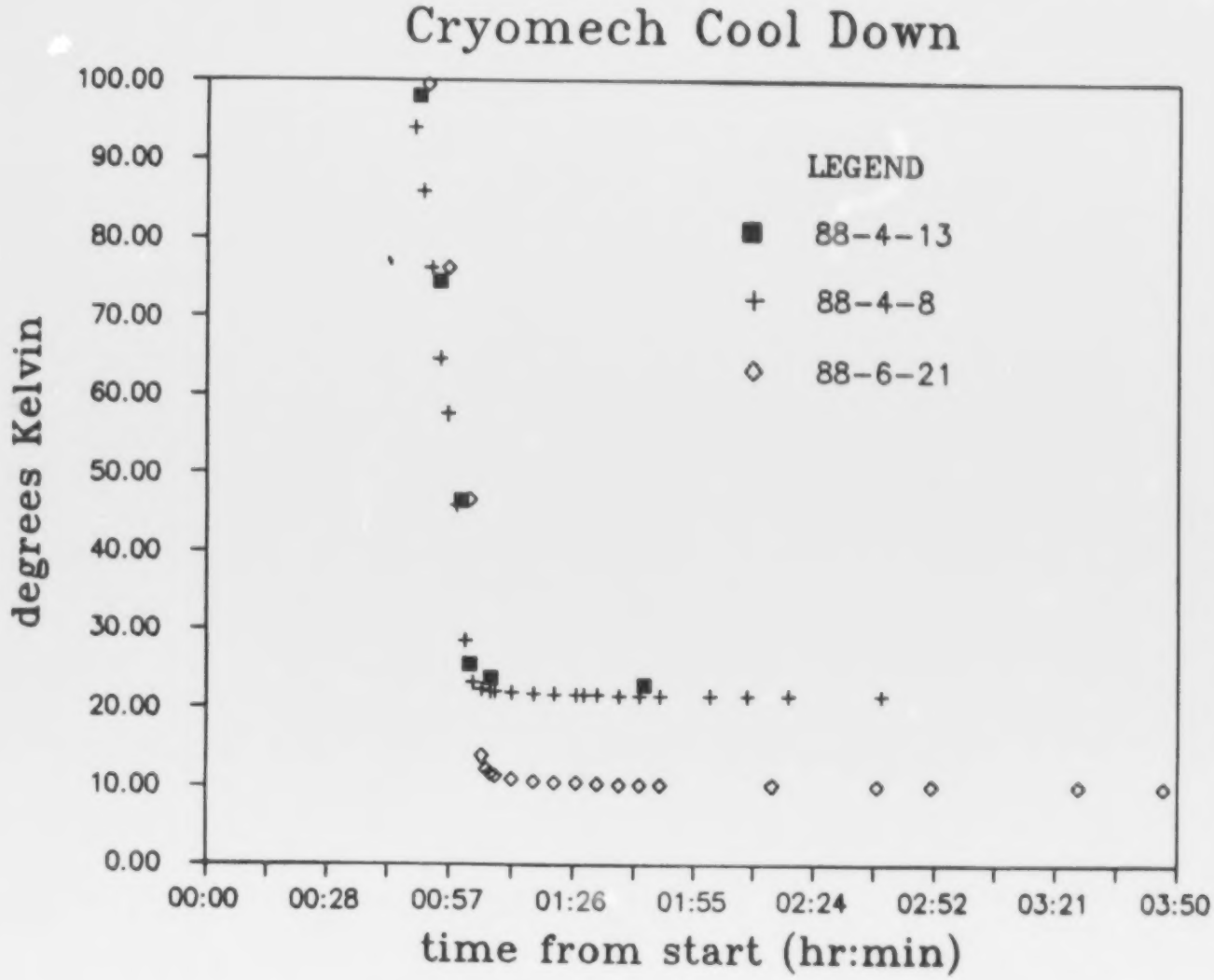
- Japanese bought He plant for 50 cm still
- Cost $250 000 US

Hydrogen Option

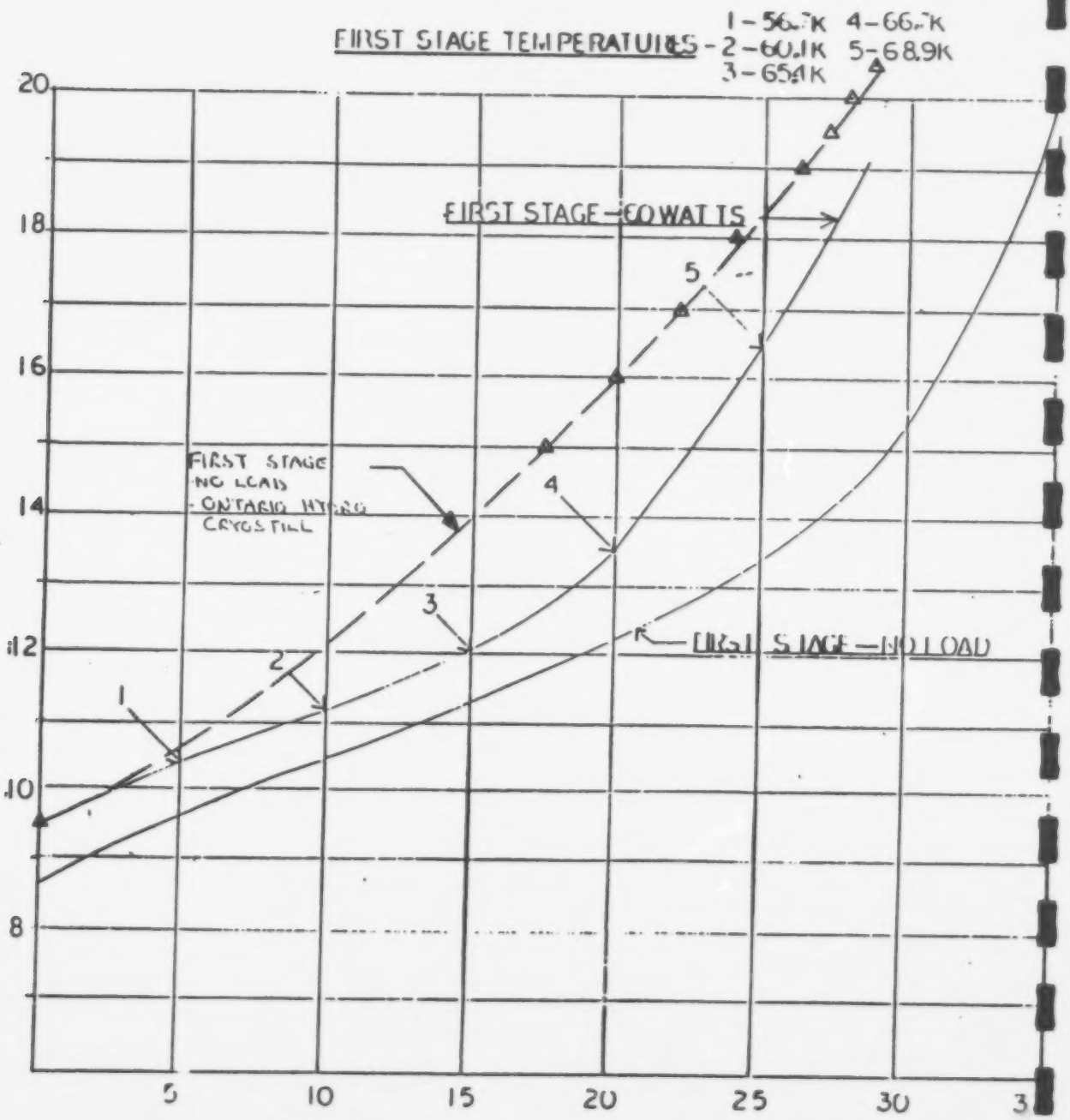
- Heat of vaporization 10 x helium
- No Canadian supplier willing to quote
- Liquid hydrogen risky to store
- Even riskier to liquefy

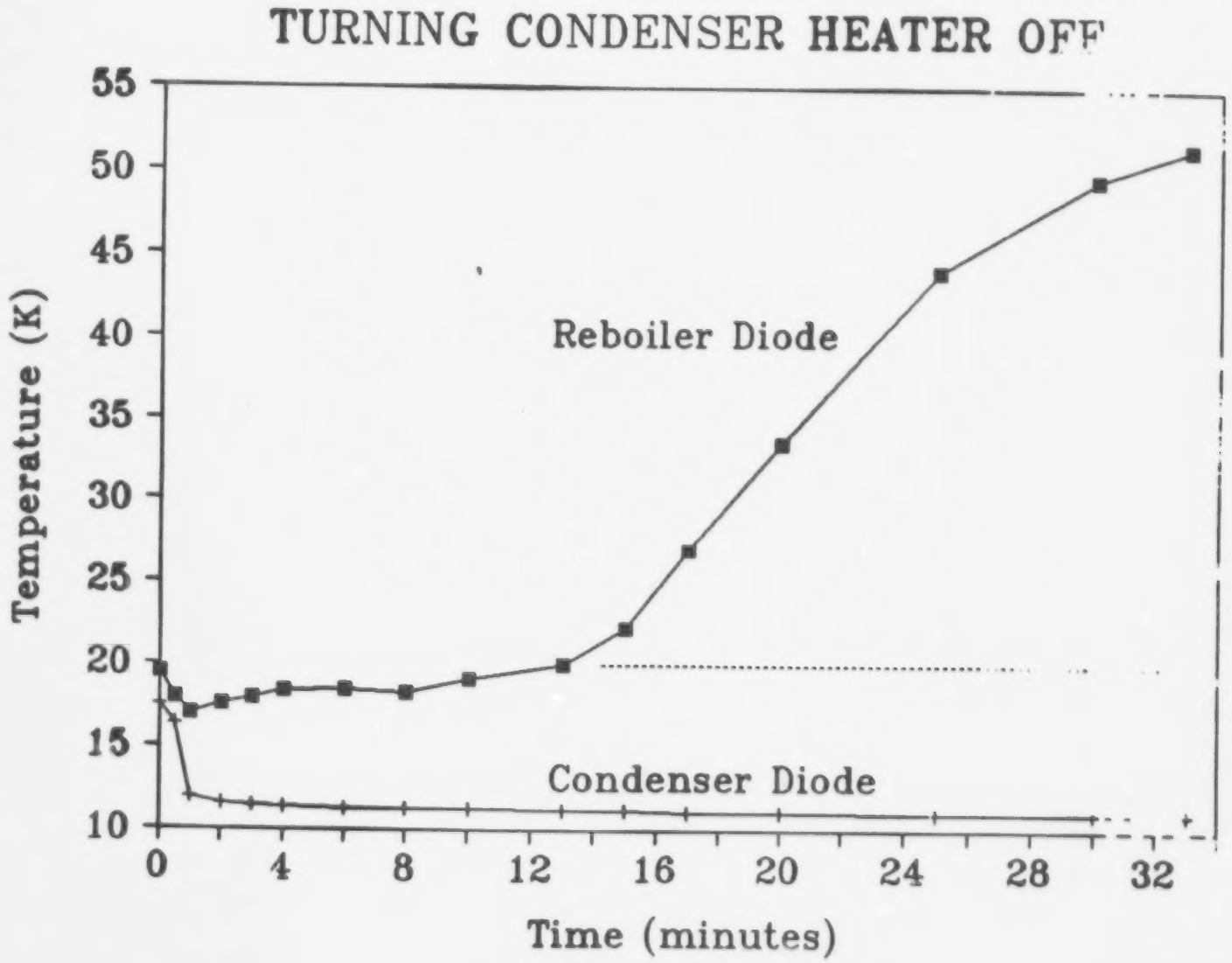
Cooling with Electricity

- Electric Coolers cool small detectors to 4 K
- Could this be scaled up?
- Market survey yielded several 10 W machines
- plus one > 30 W new machine
- Cost only $25 000 US
- No dewars needed
- for $60 000 Canadian + $30 000 labour
  - built a hydrogen isotope still
- Cost is a tiny fraction of cooling system for any liquid cryogen system
- No cryogen losses
- Operation cost - $90/week of electricity


Cryomech Cool Down
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
degrees Kelvin
LEGEND
88-4-13
88-4-8
88-6-21
00:00
00:28
00:57
01:26
01:55
02:24
02:52
03:21
03:50
time from start (hr:min)

GRAPH OF SECOND STAGE CAPACITY




TURNING CONDENSER HEATER OFF
Temperature (K)
55
50
45
40
35
30
25
20
15
10
0
4
8
12
16
20
24
28
32
Time (minutes)
Reboiler Diode
Condenser Diode

HEAT LOSSES IN STILL

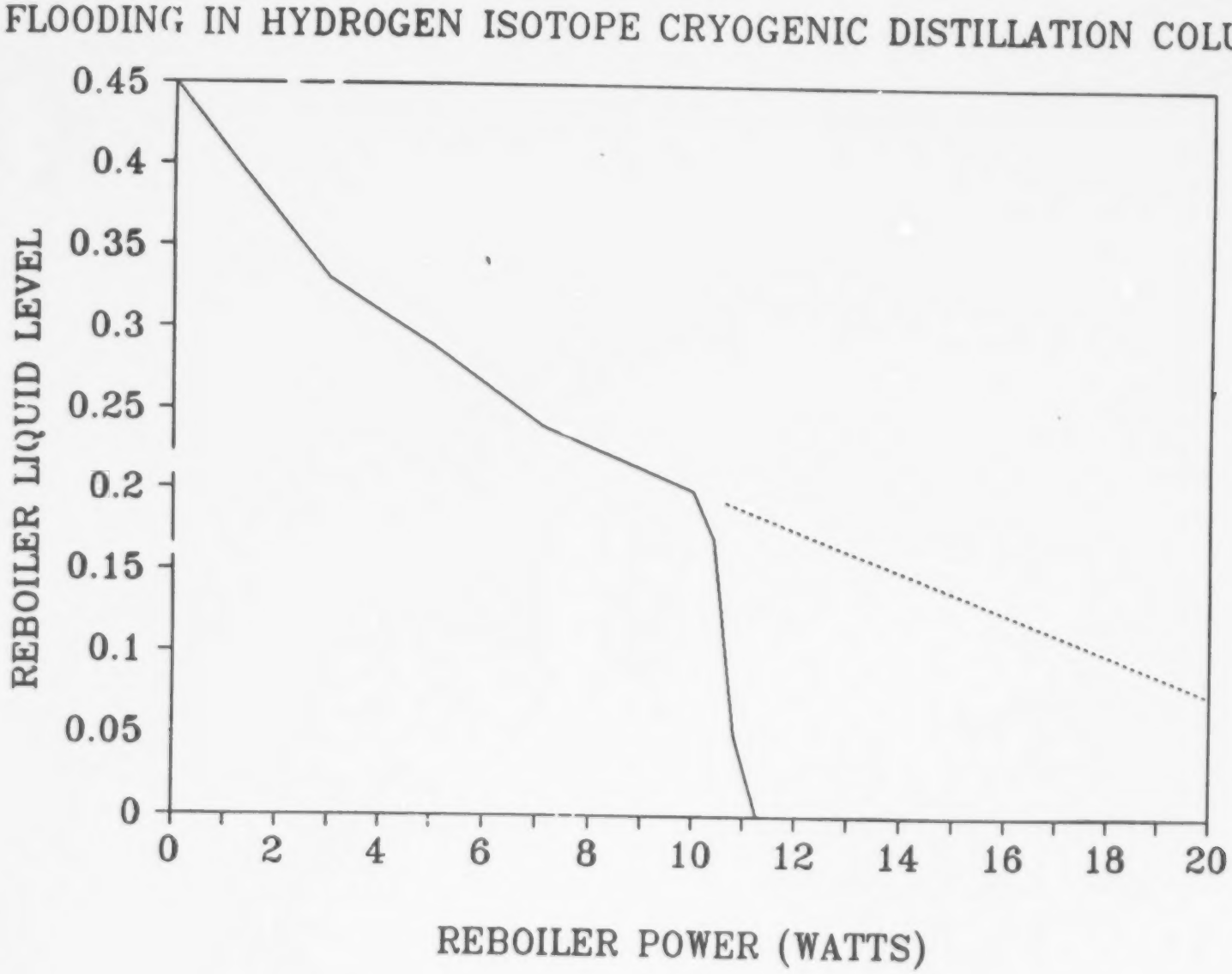
- Turning condenser heater off
- Condenser drops to 10 K
- Hydrogen starts to freeze in condenser below 14 K
- Reboiler stays at constant T for 15 min then rises slowly
- Rises after all hydrogen has boiled away

Analysis 1

- Condenser contains 112 g of copper
- After all hydrogen gone – rises slowly due to radiation
- Slope of rise predicts heat losses < 0.23 W

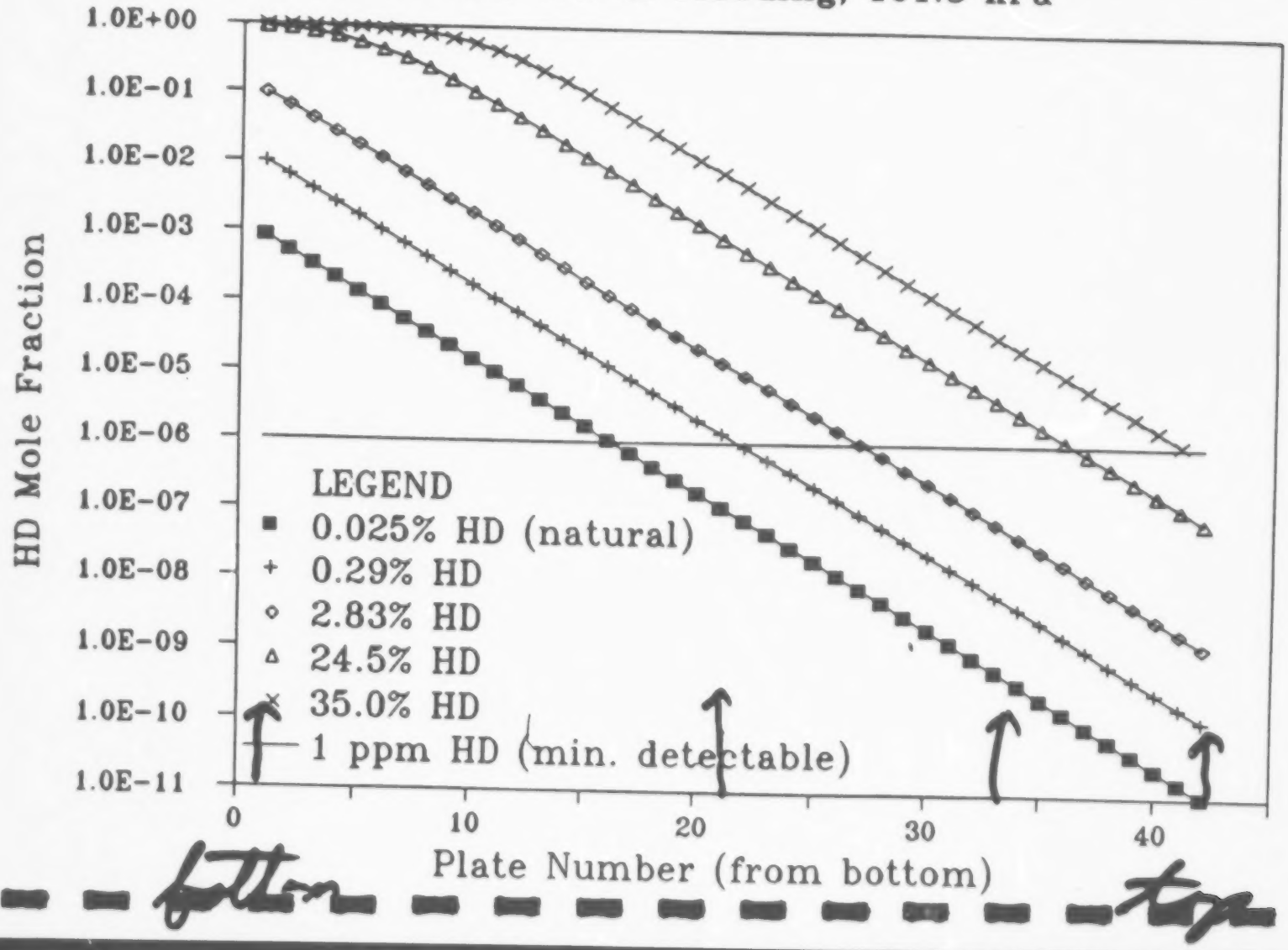
Analysis 2

- At $t = 0$ reboiler contains 0.48 g hydrogen
- 221 joules needed to vaporize this in 15 minutes
- Heat losses equal 0.246 W


FLOODING IN HYDROGEN ISOTOPE CRYOGENIC DISTILLATION COLUMN
REBOILER LIQUID LEVEL
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
12
14
16
18
20
REBOILER POWER (WATTS)

RESEARCH DIVISION HYDROGEN ISOTOPE DISTILLATION COLUMN

Total Reflux, 70% of Flooding, 101.3 kPa



SUMMARY

1. World's Lowest Cost cryogenic distillation column.
2. Built in 4 months.
3. Impressive separation power.
4. Analysis systems stressed.
5. May be possible to build small distillation systems for specific tasks rather than bringing dissimilar streams to very large cryogenic column.

OXYGEN ISOTOPE SEPARATION

J.R. Robins
Ontario Hydro Research Division

OXYGEN ISOTOPE SEPARATION

- Introduction
  - History

1773	discovered by C.W. Scheele and J. Priestly
1925	1st discovery of isotopes
1929	017 and 018 discovered in natural material

  - 3 Stable isotopes occur naturally:

016	99.7587 atom %	
017	0.0374 atom %	(0.035 – 0.041%)
018	0.2039 atom %	(0.188 – 0.209%)

Uses

- **Stable isotope hydrology and geochemistry**

  isotope distribution pattern of natural waters and geological materials

- **tracer in chemical and biological reactions**

- **NMR studies**

  O17 has a nuclear spin and a magnetic moment

- **medical studies**

  PET- positron emission tomography

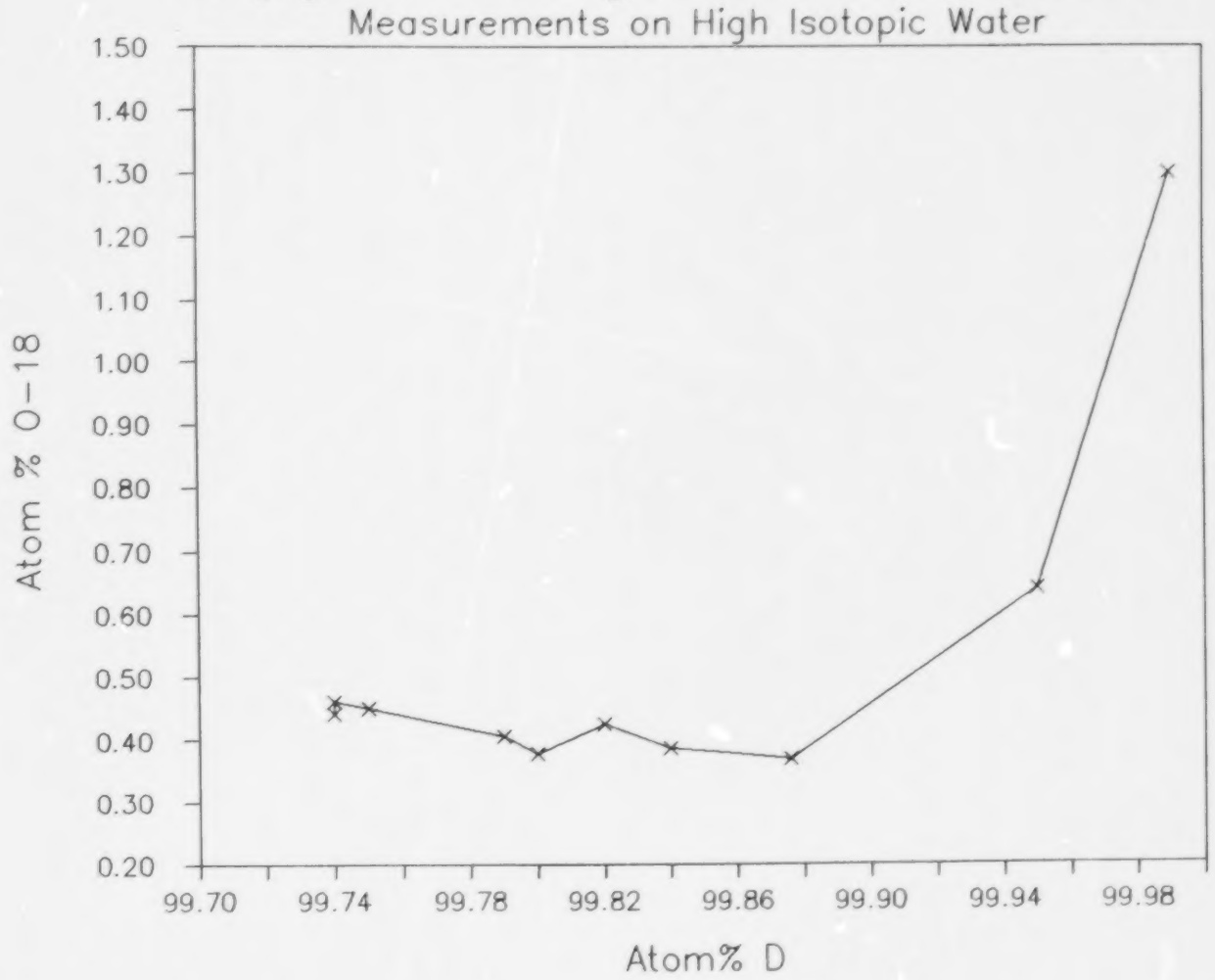
- **studies in human metabolism and energy use**

JROV2

SEPARATION METHODS

PROCESS	T(K)	ALPHA 18	ALPHA 17
H_2O distillation	350	1.0061	1.0032
D_2O distillation	348	1.0051	1.0026
CO distillation	68	1.0070	1.0036
NO distillation	121	1.0372	1.0186
O_2 distillation	63	1.01286	
$NO/H_2O/HNO_3$ exch	298	1.018	1.009
CO_2/H_2O exch	298	1.042	1.022
CO_2/D_2O exch	298	1.0259	
O_2 thermal diffusion	1073	1.016	1.008

Oxygen Isotope Measurements



JROV4

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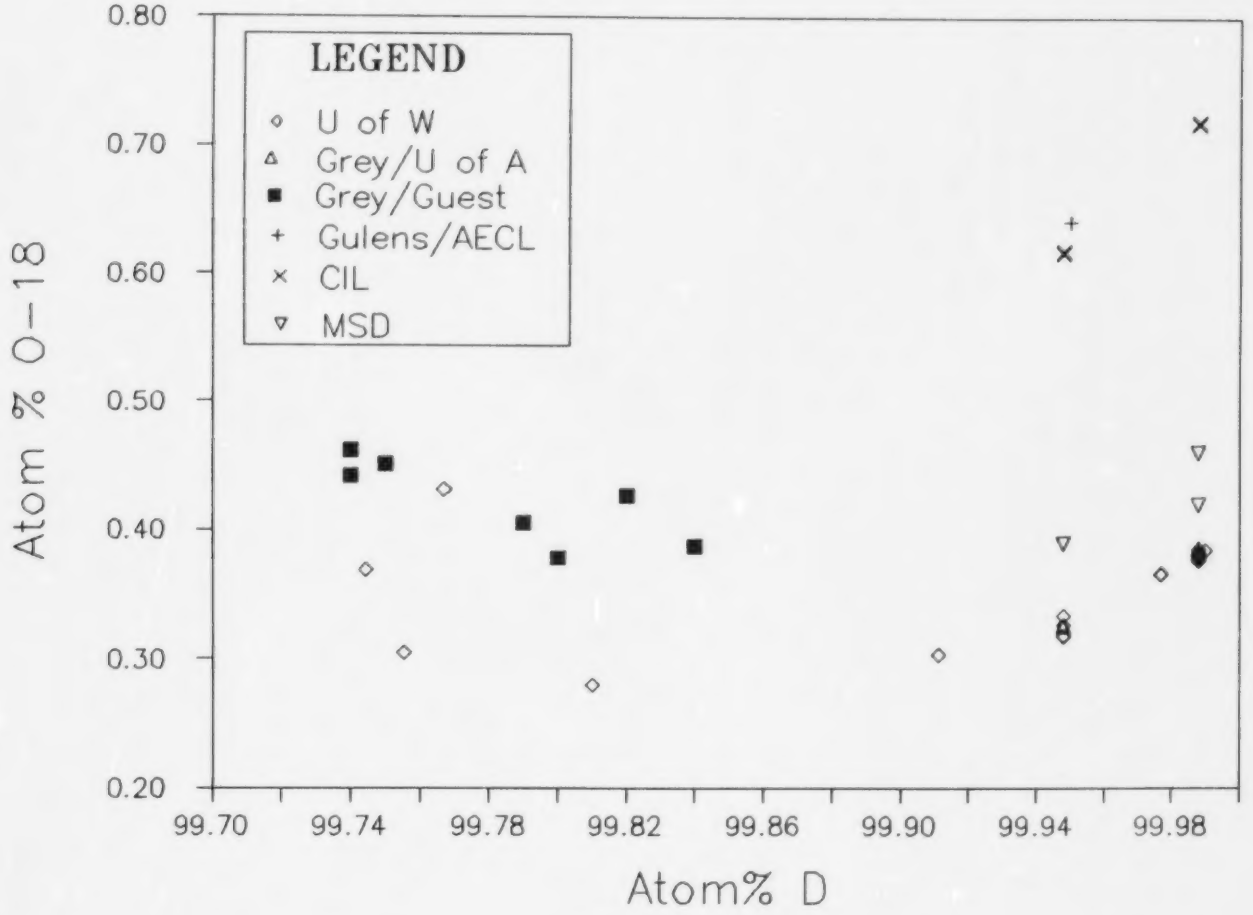
Oxygen Isotope Measurements

Measurements on High Isotopic Water



JROV5

OXYGEN ISOTOPE ANALYSIS ON WATER

- o direct injection of water into MS is not useful

- o molecular oxygen is rarely analyzed

  – difficult to produce from water with oxygen isotopes unchanged

- o conventional method is equilibration of CO_2 with water

$$CO_2(g) < > CO_2(aq)$$

$$CO_2(aq) + H_2O < > HCO_3^- + H^+$$

$$C^{16}O_2 + H_2{}^{18}O < > C^{16}O^{18}O + H_2{}^{16}O$$

- o equilibrium requires 5 hours and shaking

OXYGEN ISOTOPE ANALYSIS - CONTINUED

- equilibrium constants at 25 C:

  H_2O ALPHA = 1.0412

  D_2O ALPHA = 1.0259

  - there is a 1.5% difference

- measure mass 44, 45, 46

- standard for natural material is V-SMOW

  $^{18}O/^{16}O = 2005.20 \times 10^{-6}$

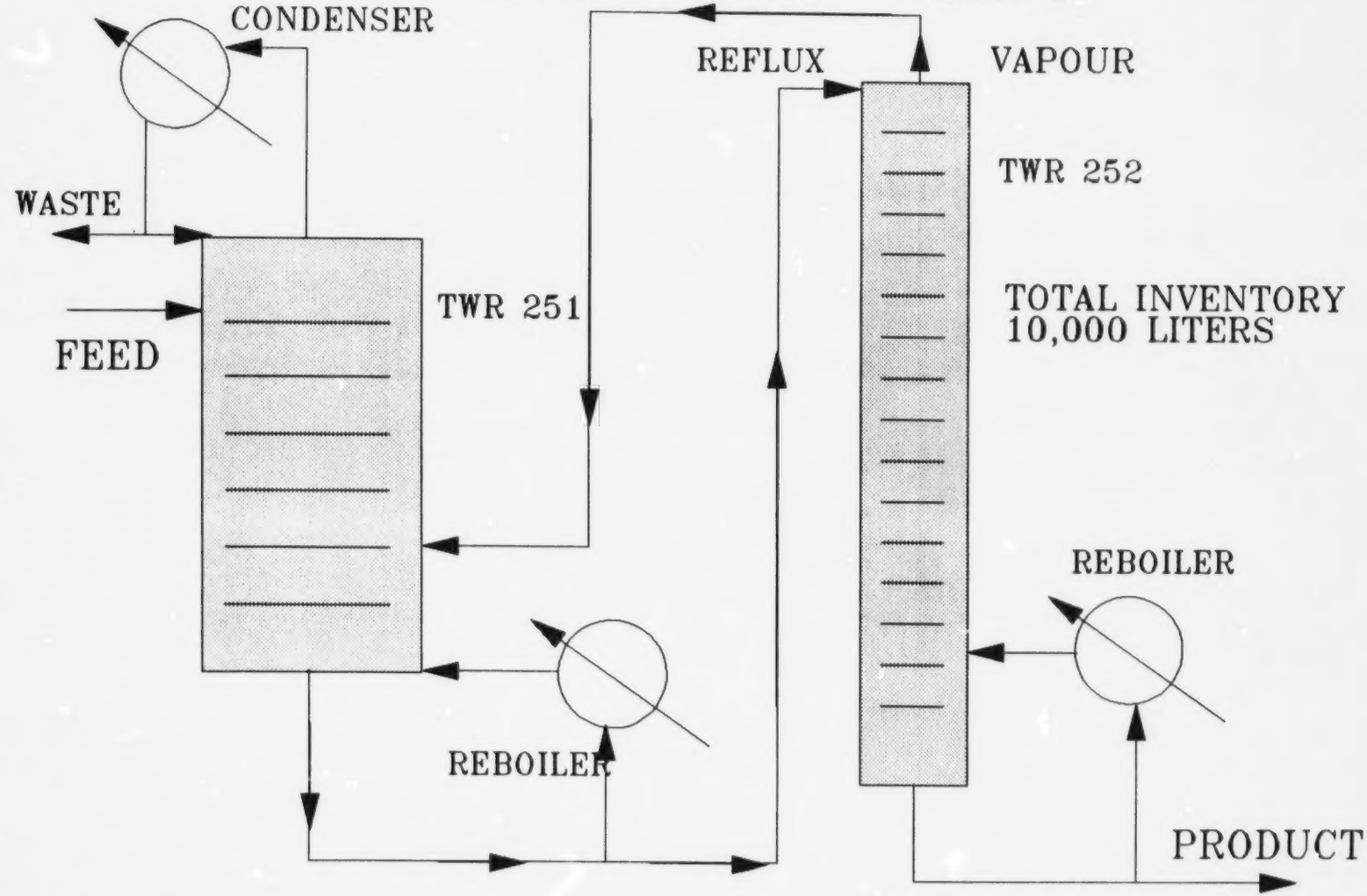
STATISTICAL DISTRIBUTION OF ISOTOPIC SPECIES OF CO_2

ISOTOPIC SPECIES	MASS	RELATIVE ABUNDANCE (%) ALL SPECIES	SAME MASS
12 16 16	44	98.40	100
13 16 16	45	1.106	93.67
12 16 17	45	7.48×10^{-2}	6.33
12 16 18	46	4.092×10^{-1}	99.79
13 16 17	46	8.4×10^{-4}	0.205
12 17 17	46	1.4×10^{-5}	0.003
13 16 18	47	4.6×10^{-3}	
12 17 18	47	1.6×10^{-4}	
13 17 17	47	1.6×10^{-7}	
12 18 18	48	4.3×10^{-4}	
13 17 18	48	1.7×10^{-6}	
13 18 18	48	4.8×10^{-6}	

UNIVERSITY OF WATERLOO MEASUREMENTS

SYNTHETIC	MEASUREMENT	% DIFFERENCE
0.323	0.334	3.41
0.418	0.423	1.20
0.893	0.915	2.46
0.893	0.918	2.80
1.152	1.112	-3.47
1.759	1.794	1.99
2.095	2.035	-2.86

F2 FINISHING UNIT – BHWP



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JROV10

THE F2 FINISHING UNIT – BHWP

- TWR 251
  - Diameter = 2.0 m
  - Height = 23.8 m
  - packed with 6 sections of BX packing

    top 3 sections have 12 layers bottom 3 have 17 layers
  - total packed height = 14.8 m
  - No of theoretical plates = 92

THE F2 FINISHING UNIT – BHWP

- TWR 252
  - Diameter = 1.6 m
  - Height = 45.8 m
  - packed with 18 sections of CY packing

    each section has 9 layers
  - total packed height = 25.8 m
  - No of theoretical plates = 309
- Total separative power = 401 stages

F2 TYPICAL OPERATING CONDITIONS

- feed rate 400 g/s
  feed conc. 20 – 30 % D_2O

  reflux flow 2.4 kg/s

- product rate 19 – 20 g/s
  product conc 99.7 – 99.9 % D_2O

- operating conditions:

	Press(kPa)	Temp(C)
condenser	8.5	45
bottom 1st tower	14.5	55
top of 2nd tower	12	57
bottom of 2nd tower	27	69

Oxygen separation constants

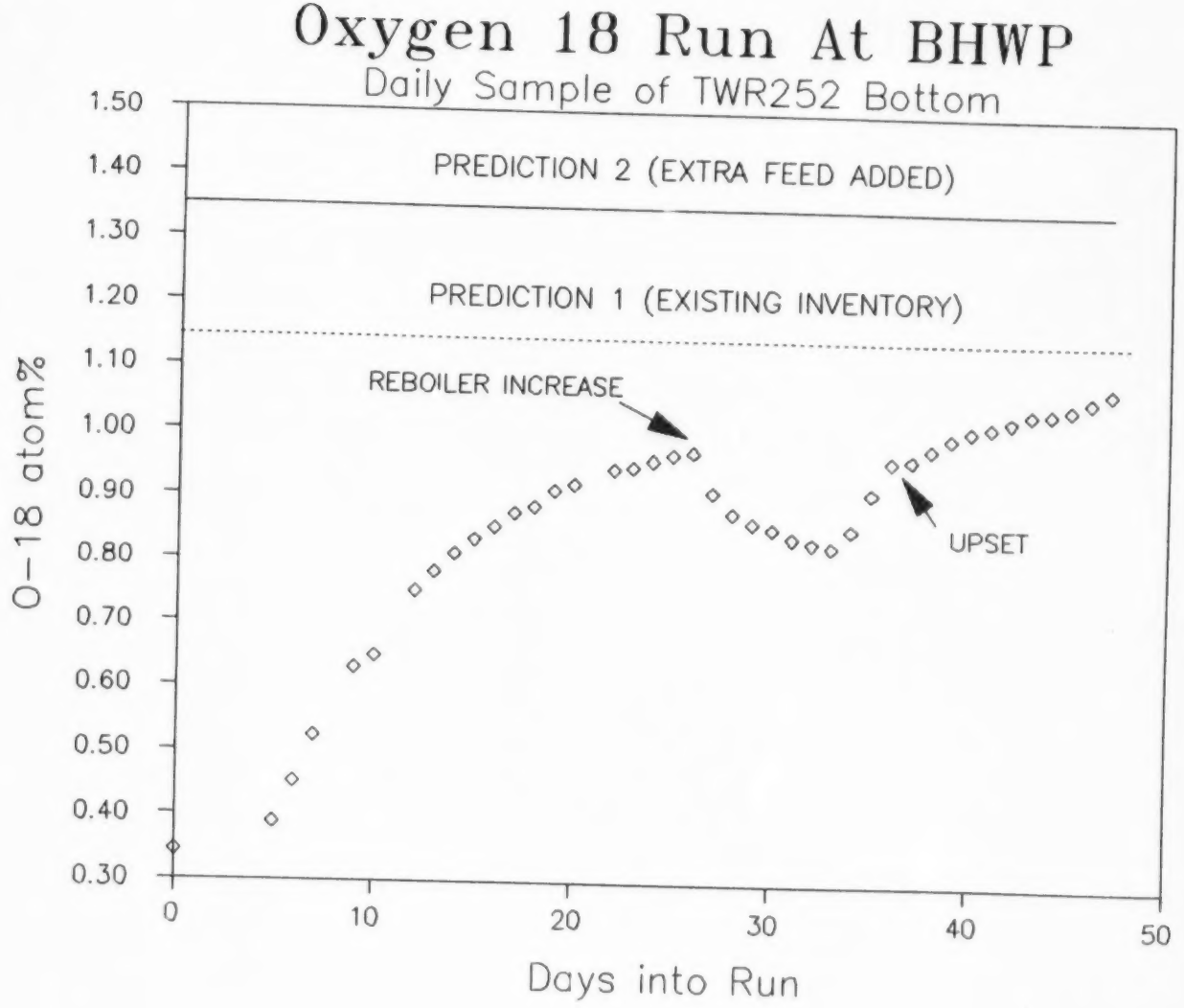
T (C)	$D_2{}^{16}O$ / $D_2{}^{18}O$
5	1.0093
25	1.0075
40	1.0071
60	1.0058
80	1.0048
100	1.0039

INVENTORY OF BASIC SYSTEM

TWR 251	125,925 moles of water
TWR 251 SUMP	64,949
TWR 252	252,282
TWR 252 SUMP	29,960
REFLUX SYSTEM	93,322
TK201	150,000

- **TOTAL 716,438 MOLES**
  (13,000 LITERS OR 14.5 Mg)

JROV14


Oxygen 18 Run At BHWP
Daily Sample of TWR252 Bottom
PREDICTION 2 (EXTRA FEED ADDED)
PREDICTION 1 (EXISTING INVENTORY)
REBOILER INCREASE
UPSET
O-18 atom%
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0
10
20
30
40
50
Days into Run

SIMULATIONS OF THE F2 UNIT WITH OXYGEN 18

- **spread sheet calculation**
  - 401 plates based on Fenske using temp profile
  - calculated concentration of 018 /plate
  - summed tower inventory
- **Total inventory of 018 in tower**
  - 14.3 Mg @ 0.344 atom % 018

    = 2464.5 moles 018

- Adjust the concentration of the feed tray until Fenske predicts a concentration profile that adds up to 2464 moles 018

- Equilibrium condition = 1.15 atom% 018

- An additional 4 Mg of water will be added with 4 Mg removed from the top of the 1st tower

- Equilibrium condition = 1.35 atom% 018

WHERE DO WE GO FROM HERE

- **Maximum concentration possible in F2 with a feed of 0.34% is**
  - 2.6 atom % O18
- **Collect product and use as feed**
- **Collect product and develop smaller scale system**
  - CO distillation with Research still
  - Water distillation with small still
  - Develop exchange technique with CO2

jrov19

USE OF TUNABLE DIODE LASERS AS SENSITIVE DETECTORS OF ISOTOPE RATIOS

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TO BE PRINTED AND DISTRIBUTED LATER AS AN ADDENDUM TO

THIS REPORT NO 89-49-K.